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THE COLOR CORRECTION OF AN ACHROMATIC DOUBLET. II.

By T. Townsend Smith

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About two years ago I published in this Journal a paper with the same title as the present one,[1] and in that paper I presented the results of some calculations on the damage done to an image by the secondary spectrum of an achromatic doublet. The work was based upon a color curve deduced with the help of the Hartmann interpolation formula

$$n = n_0 + \frac{c}{\lambda - \lambda_0} \tag{1}$$

and the results were expressed in terms of a "visual efficiency," which is the ratio of the visual intensity on the axis of the lens to the intensity which would be obtained with a perfectly achromatic lens. The effect of spherical aberration upon the efficiency was entirely neglected—as it is in the present work.

The results of the work just referred to gave the visual efficiency as a function of the dimensions of the lens, it being assumed that the doublet consisted of a converging silicate crown lens (Schott 0–60) and a diverging lens of dense flint (Schott 0–103). The present work deals with the effect upon the visual efficiency of a change in the relative

[1] J.O.S.A. & R.S.I., *10*, p. 39; 1925

powers of the two component lenses, brought about either by changing the curves of the lenses or by varying the constants of the glasses.

I. TWO CORRECTIONS TO THE PREVIOUS WORK

There were two serious errors in the earlier work. One of these resulted from a mistake in multiplying, the number 2028, next to last line of page 56, being incorrectly used for 2128. All of the values of the visual efficiency in the table at the top of page 57 and all of those plotted in Fig. 10, except obviously 1.00, should, therefore, be reduced in the ratio 2028/2128, or about five per cent. Evidently the relative values of the table are not affected by this change. The other error was due to my ignorance of the energy distribution in black body radiation. The figures in column VII of Table 2 were used as giving the relative values of the rate of emission of energy, whereas the figures

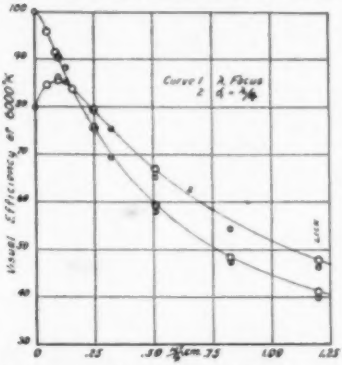

FIG. 1.—*The relation between visual efficiency and the dimensions of the doublet. Points designated by the larger circles are for* $\lambda_1 = 560\ m\mu$, *and by the smaller circles for* $\lambda_1 = 550\ m\mu$.

should be used as a measure of the physiological effect of this energy upon the eye. The figures in column VIII are thus incorrect, as these should be the product of the figures of columns IV and VII, instead of VI and VII as given in Table 2. This error affects also curve 3 of Fig. 5, all of the numerical values of the efficiency in section IV and all of the values of Fig. 11.

Fig. 5 I have not redrawn, but the corrected Fig. 11 is Fig. 1 of this paper. Corrected figures for the numerical results of section IV are shown graphically in the two lower curves of Fig. 2 of the present paper, from which it appears that the visual efficiency of the pseudo-Lick telescope is even lower than the values given in section IV. It appears also from the corrected values shown herewith in Fig. 1 that

the figures at the top of page 60 are those for a visual efficiency of 80 per cent and not 90 per cent, and that the last paragraph of section V should be changed to make the value of $(2H)^2/\mathcal{F}$ not over one-half instead of not over one, as is there indicated.

II. THE EFFECT OF A CHANGE IN THE COLOR CURVE

The color curve for a lens gives the proportional change in the focal length ($\mathcal{F}$) in its dependence upon the wave length of the light. For an achromatic doublet made from any of the usual glasses, the form of the color curve is that shown in Fig. 3 of this paper or in Fig. 1 of the previous paper. For a particular choice of glasses the color curve will depend upon the relative powers of the two lenses which form the doublet, and it is necessary to use some criterion for specifying the particular color curve which will be exhibited by a given doublet. This is commonly done by specifying the two wave lengths at which the focal length of the doublet is to have the same value, as for example the *C* and *F* hydrogen lines. For the present work it is more conveniently done by specifying the wave length (λ_1) at which the doublet has a minimum focal length. The relation between these two criteria is indicated by Fig. 2 of the previous paper.[2]

As a parameter to designate the dimensions of the lens, I have used the quantity $H^2/\mathcal{F}$, as in the preceding paper. Here H designates the radius of the lens aperture and $\mathcal{F}$ the focal length of the doublet, which is calculated on the assumption of thin lenses in contact. The reason for using this quantity ($H^2/\mathcal{F}$) is (loc. cit., section V) that the dimensions of the lens enter in this form into the expression for determining the visual efficiency of the lens.

Two values of $H^2/\mathcal{F}$ were selected as reasonable ones, which would be likely to be significant in lens design, these values being 0.10 cm and 0.25 cm. These values are, I believe, in the range which is in common use for small lenses. The 6×30 prism binocular has objectives with focal lengths of about fifteen centimeters. This would make $H^2/\mathcal{F}$ equal to $(1.5)^2/15$ or .15 cm. For a focal length of 15 cm and a value of $H^2/\mathcal{F}$ equal to 0.10, the clear aperture would be just under 2.5 cm. The telescope of a certain transit has an objective of clear aperture about 3.3 cm and a focal length of just under 20 cm. $H^2/\mathcal{F}$ for this objective is about 0.14 cm. I have by me a telescope, the clear aperture of which is 3.3 cm and the focal length of the object glass about 35 cm. $H^2/\mathcal{F}$ figures out to be about 0.08 cm for this lens. A lens has been described to me as one with large aperture and good per-

[2] Cf. also Nature, 114, p. 536, 1924.

formance, the dimensions being 8.25 inches (21 cm) focal length and 1.5 inch (3.8 cm) aperture. The value of the parameter $H^2/\mathcal{F}$ is a little over 0.17 for this lens.

The type of achromatism and the dimensions of the lens are sufficiently specified by the two parameters λ_1 and $H^2/\mathcal{F}$, but these are not sufficient to calculate an optical efficiency. There is necessary in addition (1) a color sensitivity curve for the eye or for the photographic plate (if that be used), and (2) a knowledge of the spectral distribution

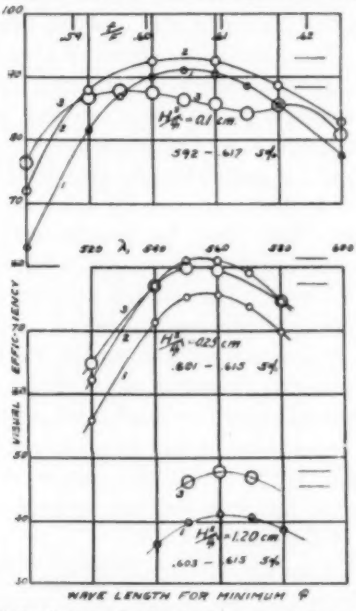

FIG. 2. *The relation between the visual efficiency and the type of achromatism; λ_1 is the wave length of minimum focal length.*

of energy in the light given out by the source. In the present work the color sensitivity values for the eye were taken from Mr. Priest's curves,[3] and the source was assumed to be a black body at a temperature of 6000° Kelvin. The results would be but little different if a constant value were assumed for the rate of energy emission (E_λ) within the range of the spectrum which is here significant.

With these assumptions I have calculated the visual efficiency for the two values of $H^2/\mathcal{F}$ for various values of λ_1, and the results of this

[3] Scientific Papers of the Bureau of Standards, No. 417; 1921.

calculation are shown in Fig. 2, where there is added the corrected values for a telescope of the size of the Lick Observatory refractor, as indicated in the preceding section.

In each of the three sets of curves, curve *1* gives the visual efficiency for a point on the axis at the λ_1 focus. Curves *2* and *3* are for points a little further from the lens, for which the values of the phase angle α are respectively 0.4 and 0.8 radians for the wave length λ_1, the angle α being determined by the equation (cf. equation 17, loc. cit.)

$$\alpha = \frac{\pi}{2} \cdot \frac{1}{\mathcal{F}} \cdot \frac{\delta \mathcal{F}}{\lambda} \cdot \frac{H^2}{\mathcal{F}} \tag{2}$$

and being defined as the half of the phase difference between the axial and the peripheral rays. For curve 2 this phase difference would be, therefore, 0.8 radian and for curve *3* 1.6 radians, equivalent to path differences of $\lambda_1/8$ and $\lambda_1/4$ respectively. In the two sets of curves corresponding to values of $H^2/\mathcal{F}$ of 0.10 and 0.25 it is clear that at least for the central portion of the region represented, curve *2* gives very nearly the maximum efficiency. For the pseudo-Lick objective of the third set of curves, curve *3* represents very nearly the maximum, as may be seen from Fig. 8 of the preceding paper.

The second scale shown at the top of Fig. 2 gives the ratio of the focal lengths of the two lenses for the *D* lines, the values being calculated from Hartmann's formula. The formula for this calculation is

$$\frac{f}{F} = \frac{N_D - 1}{n_D - 1} \cdot \frac{\rho}{P} = \frac{N_D - 1}{n_D - 1} \cdot \frac{c}{C} \frac{\lambda_1 - \lambda_0}{\lambda_1 - \Lambda_0} \tag{3}$$

the second equality of this formula following from a combination of equations (4) and (7) of the previous paper. This procedure gives values for the ratio of f/F which are somewhat different from the values of the ratio calculated directly from the indices. For example, for a *C–F* correction the value of the ratio as calculated directly is just under .603 and as calculated from the interpolation formula about .605. It is somewhat difficult to estimate the significance of this variation. Essentially this same difference reappears in the attempt to interpret the results represented in Fig. 2.

III. TOLERANCE LIMITS FOR THE RATIO *f/F*

I have tried to interpret the results represented in Fig. 2 in two different ways. In the first place, I have assumed that the visual efficiency may decrease by five per cent of its maximum value without the difference being particularly noticeable, and with such an assumption one may write down immediately the limits within which the

value of λ_1 or of the ratio f/F must be held. The five per cent limits are indicated on the figure, and from the figure one may write down the permissible variation as follows:

Value of $H^2/\mathcal{F}$	0.10	0.25	1.20
Limits for λ_1 (mμ)	521– 582	540– 575	548– 576
Limits for f/F	.592–.617	.601–.615	.603–.615

There is probably no peculiar virtue in using five per cent as a criterion, and if it be assumed that ten per cent is a permissible decrease in the efficiency, then the limits for λ_1 and for f/F may be increased somewhat. The figures obtained in this manner would, in either case, represent the permissible variations within which the powers of the two lenses of a doublet may be varied, the glasses used being always the same. The calculations are based on Schott 0–60 and 0–103, but I think it will be found that the permissible variation will be about the same for other combinations.

IV. TOLERANCE LIMITS FOR THE CONSTANTS OF THE GLASSES

In making a second attempt to interpret the results of Fig. 2, I have tried to solve the problem as to how much a change in the constants of the glasses used for the doublet would affect the visual efficiency. This is a more difficult problem, for it involves the question as to how much a change in these constants would affect the color curve of the doublet. Quite obviously if the color curve should change appreciably with a change in the type of the optical glass, then fresh calculations will need to be made from the beginning. The whole calculation depends upon the shape of this curve, which represents the change in the focal length of the doublet as a function of the wave length.

1. *Color Curve and Types of Glass.* Fortunately it appears that a change in the glass produces a very small change in the shape of the color curve. The evidence in favor of this assertion is given in Fig. 3. The curves of this figure are drawn to fit equation 10 (p. 45, loc. cit.), the values of the constants being those there given, and the whole being based upon the assumed validity of the Hartmann dispersion formula in its simpler form. The points are obtained by direct calculation from Gifford's and Hopkinson's measurements of indices of refraction.

The formula for this calculation is simple and it is easily obtained. The resultant focal length for a thin lens doublet is*

$$\frac{1}{\mathcal{F}}=\frac{1}{f}+\frac{1}{F}=\frac{n-1}{\rho}+\frac{N-1}{P} \tag{4}$$

* The lower case symbols refer to the crown lens and the capitals to the flint lens.

and the variation in the focal length is

$$\delta\frac{1}{\mathcal{F}}=-\frac{\delta\mathcal{F}}{\mathcal{F}^2}=\frac{\delta n}{\rho}+\frac{\delta N}{P} \tag{5}$$

From these two equations one gets

$$-\frac{\delta\mathcal{F}}{\mathcal{F}}=\frac{\delta n}{(n-1)+(N-1)\frac{\rho}{P}}+\frac{\delta N}{(N-1)+(n-1)\frac{P}{\rho}} \tag{6}$$

where the ratio of the rhos is determined by the ratio of $(n-n')$ to $(N-N')$, the indices corresponding to wave lengths λ and λ'. For curve *1* the doublet is supposed to have the same focal length for the *F* line and the red lithium line, 486 mμ and 671 mμ and for curve *2* for the *F* and *C* hydrogen lines, 486 mμ and 656 mμ.

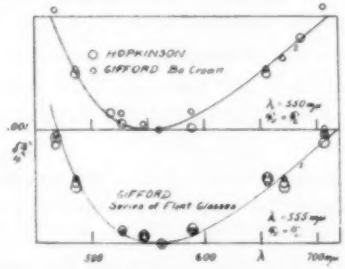

FIG. 3. *The relation between the color curve and the types of glass used in the doublet.*

The four sets of points plotted on curve *1* correspond to combinations of four different dense flints with a single hard crown, the focus for the lead line (561 mμ) serving as a zero from which is calculated in each case the change in focal length of the combination. The dispersion constant for the hard crown is 59.95 and for the flints 37.72, 37.05, 36.46, and 36.29 respectively, with corresponding nD values of 1.5197, 1.6046, 1.6107, 1.6190, and 1.6229.[4] That the glasses all give essentially the same color curve and that this curve is well represented by the one drawn with the aid of the interpolation formula is, I believe, apparent.

For curve 2, the smaller circles refer to a combination of the lightest of the dense flints just referred to with a barium silicate crown, $\nu=57.44$ and $nD=1.5714$,[5] and the larger circles refer to an ordinary crown and dense flint of Hopkinson.[6]

[4] J. W. Gifford, PRS, A, *100*, p. 621; 1921.
[5] J. W. Gifford, PRS, A, *87*, p. 189; 1912.
[6] Hopkinson, PRS, *26*, pp. 293, 296; 1877.

Within the significant range, that is, perhaps between the C and the F lines, the greatest variation is that of the D line of Hopkinson's series. The difference between curve and point is about .00008. Suppose that we assume this difference to be caused by an inaccuracy in the measured index of the crown glass and that we seek to determine the requisite inaccuracy. This can be easily found by the aid of the formula with which the value was calculated

$$\frac{\delta \mathcal{F}}{\mathcal{F}} = -\frac{\delta n}{.20812} + \frac{\delta N}{.41924} \tag{7}$$

The inaccuracy is .000016, which is probably not much greater than the experimental error of the determination.

2. *Types of Glass and Types of Achromatism.* Assuming then that the color curve will not change with the constants of the glasses, I have attempted to solve the problem at issue under the following form: If it be assumed that the curves of the lenses are to be fixed and that a change is to be made in the glass, then, on the basis of the results represented in Fig. 2, to what extent will this change affect the visual efficiency?

The radii of curvature do not enter directly into the calculations, but the quantities ρ and P do, and for our present purpose it is sufficient to require that the ratio ρ/P shall be constant. What we require is for each pair of glasses a relation between the quantity ρ/P and the parameter λ_1, inasmuch as we know from Fig. 2 the way in which the parameter λ_1 is related to the visual efficiency.

As constants of the glasses I have used the figures given by Czapski in his first publication on the Jena glasses[7] for the following types of glass:

Type of Glass	nD	Dispersion Constant
Flint glasses		
Schott 0–118	1.6129	36.9
0–167	1.6169	36.5
0–103	1.6202	36.2
0– 93	1.6245	35.8
Crown glasses		
Schott 0– 57	1.5086	61.8
0– 60	1.5179	60.2

The ratio of the partial dispersions for a given region and for a particular crown and flint combination is equal to the ratio of ρ to P,

[7] ZS. Instk., 6, p. 335; 1886.

and inasmuch as Czapski gives the partial dispersions for the regions A'–F, C–F, D–F, and D–G', the values of ρ/P are thus given for these particular regions. Then from Fig. 2, p. 46 of the earlier paper on *Color Correction*, or some curve similarly drawn, one obtains the value of λ_1 for the various regions. These two sets of figures give the needed relation between λ_1 and ρ/P for the various combinations of glasses. The results are represented in Fig. 4.

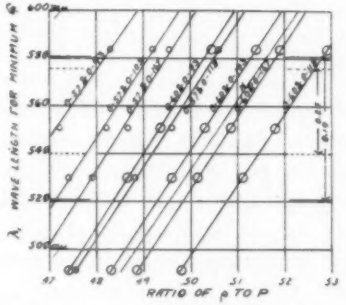

FIG. 4. *Relation between the ratio ρ/P and the parameter λ_1 for various combinations of glasses.*

The table below, for the combination of glasses 0–60 and 0–103, should serve to make clear the manner in which the results of Fig. 4 are obtained.

Spectrum Range mμ	A'–F 768–486	C–F 656–486	D–F 589–486	D–G' 589–434
Partial Dispersion				
0–60	1158	860	605	1092
0–103	2254	1709	1220	2261
Ratio or ρ/P	.514	.503	.496	.483
Value of λ_1 in mμ	584	551	530	491

In Fig. 4 the two full lines parallel to the axis of ρ/P represent the limits of the permissible variation in λ_1 on the five per cent criterion and for an $H^2/\mathcal{J}$ value of 0.10, and the two broken lines represent the limits for an $H^2/\mathcal{J}$ value of 0.25 on the same criterion. If, then, for a particular pair of glasses and for a particular set of radii of curvature, the value of λ_1 lies within the limits specified, one may conclude on the basis of the criterion adopted that the color correction will be satisfactory.

3. *Illustrative Example.* The frequently used combination of a double convex crown with a plano concave flint will serve as an example. For such a combination the ratio ρ/P has the value .500. For the various glasses represented, and for the $H^2/\mathcal{J}$ value of 0.10, the visual efficiencies are as follows:

Crown Lens	0–60	0–60	0–60	0–60	0–57	0–57
Flint Lens	0–93	0–103	0–167	0–118	0–118	0–167
λ_1 in mμ	570	543	526	497	566	597
Visual Efficiency	.91	.93	.90	.77	.92	.84

The other two combinations give values for λ_1 which are outside the range of my calculations. As the maximum efficiency for this aperture is about .93, on the five per cent basis efficiencies above about .88 would be satisfactory, and hence any of the combinations here listed should be satisfactory, except 0–60 and 0–118, and 0–57 and 0–167.

4. *A Restriction on the Application of Hartmann's Formula.* There is a restriction which will modify somewhat the numerical results given in the preceding paragraph. The λ_1' values represented in Fig. 4 are all obtained from a color curve calculated from Hartmann's formula, whereas the values of ρ/P are calculated directly from the measured values of the indices. This last calculation can also be based upon Hartmann's formula, and the two calculations do not quite agree. I have calculated the Hartmann curve for 0–60 and 0–103 and this is drawn as a dashed line, marked *H* in the figure. Which of the two is the more nearly correct, I do not know, nor do I know of any measurements of indices which have been made with sufficient accuracy to decide the question. In any case, I think one would be safe in concluding that the differences just referred to in the calculated values of ρ/P will not affect the results in so far as they relate to the permissible variation in the glasses used, for differences of the sort referred to would be expected to exist in all of the combinations to about the same amount.

THE BRACE LABORATORY OF PHYSICS,
LINCOLN, NEBRASKA

ON THE INFRARED ABSORPTION SPECTRA OF SEVERAL GASES

By C. F. Meyer, D. W. Bronk, and A. A. Levin

ABSTRACT

The spectra of acetylene, ethylene, *n*-butane, *n*-hexane, *n*-octane, benzene, toluene, cumene, ethyl alcohol, ethyl ether, and sulphur dioxide were investigated with a grating of 1134 lines per cm in the region between 3 and 4 μ. The absorption curves are represented in figures. A table gives the wave-numbers of the maxima and selected wave-number differences. The individual lines of the bands are not revealed, but the envelopes are obtained. From the latter an attempt is made to state what branches are present in the bands. Attention is called to relations existing among the wave-number differences.

The diffraction grating has repeatedly proven its value in disclosing detail of structure of absorption bands in the infrared, but the number of spectra which have been investigated by means of it is relatively small. The authors undertook the present work because they felt that additional spectra should be examined. The spectra of the hydrocarbons show interesting similarities when examined with a prism,[1] and it was decided to begin an examination of some of these with a grating. It was desired to study the compounds of simple structure so far as possible, but these could not always be obtained or easily made. As a consequence the list of compounds here given is a somewhat heterogeneous one. Ethyl alcohol and ethyl ether were included simply because they were at hand, and sulphur dioxide was studied because it could be easily made, and because of its relation to carbon dioxide which has received much attention from various investigators.

The work was undertaken as a preliminary step in attacking a new field, with the idea of following up more completely any particular problem which might develop. Such a problem has developed in the examination of the spectra of acetylene, ethylene, and ethane which is now under way.[2] The results of the preliminary work which are to be here reported, are fragmentary, but they contribute to our knowledge of the spectra in question and reveal the complexity of structure of bands which are recorded as simple ones with a prism spectrometer.

A spectrometer and grating were at hand which were suitable for work in the region lying between 3 and 4μ, and therefore the spectra were examined in this region. A fore-prism served to exclude the second

[1] Coblentz, W. W., Publications of the Carnegie Institution of Washington, 35; 1905.
[2] Meyer, C. F., and Levin, A. A., Proc. Nat. Acad. of Sc., *13*, 5, p. 298; 1927.

and higher spectral orders. The grating was one of 1134 lines per cm (2880 lines per inch) ruled on aluminum.

The first data were obtained over four years ago, and were reported to the Physical Society.[3] The results were not published in detail as it was feared they might contain errors due to interference bands produced by the mica of the cell windows, and this in fact proved to be true. A method was subsequently found of eliminating these errors,[4] and certain discrepancies between the results now given and the report referred to above are due to their elimination.

An effort was made to secure pure chemical compounds, but no attempt was made to analyze them. There is a possibility that one or more of the minor features in the curves are due to impurity, but it is believed to be a remote one.

The curves which are reproduced below each represent one series of observations, that is, a single "run." In beginning work with a new compound an exploratory run is necessary; for this, observations were made while setting the circle of the spectrometer at intervals of five minutes of arc. Thereafter several runs were usually made at intervals of one minute of arc (50 AU). Repetition is desirable in order to eliminate accidental errors, and moreover the clearness with which the structure of a band is revealed depends upon the amount of gas in the path of the beam, and it is well to make successive runs with different amounts. By a study of the curves obtained in several runs, it is possible to decide upon the real characteristics of the absorption, and relegate certain minor maxima, which occur in a single curve, to the limbo of accidental error. The curves reproduced are those which it is felt best represent the absorption for each gas. They were drawn through each point obtained in the run selected, and consequently include all of the observational error of that run. Broken lines have been inserted where it is believed that the particular run which is represented is in error, the broken line indicating the corrected curve. Short vertical arrows have been placed below the maxima which are believed to be real, and a number has been placed below each arrow for purpose of reference to the maximum in question.

Table 1 gives the wave numbers of the maxima which are arranged in columns according to the aforementioned numbers under the arrows. Wave-number differences between selected maxima are also given. The decimal portion of the wave number, given in cm^{-1}, has been retained

[3] Meyer, C. F., and Bronk, D. W., Phys. Rev., *21*, 6, p. 712; 1923.
[4] *Idem*, Astrophys. Journ., *59*, 4, p. 252; 1924.

though it carries little weight, especially where the maxima are broad or the slopes are different on the two sides.

The definition attained, as determined by the slit widths and by the grating space, is not sufficient to resolve the absorption bands into

TABLE 1.

Wave numbers (per cm) of the maxima of absorption as numbered in Figs. 1, 2 and 3 and selected wave-number differences.

Name of gas	Number of maximum				
	1	2	3	4	5
Acetylene	3267.8	3308.9			
		41.1			
Ethylene	2965.5	2990.1	3015.1	3085.1	3127.7
		49.6		42.6	
n-Butane	2883.5	2897.5	2968.7	2982.0	
		14.0	13.3		
n-Hexane	2877.2	2938.8	2971.6		
		61.6	32.8		
n-Octane	2868.0	2934.4			
		66.4			
B nzene	3051.5	3096.5			
		45.0			
Toluene	2888.1	2937.1	3040.4	3075.7	
		49.0	35.3		
Cumene	2896.0	2943.1	2973.8	3040.8	3074.8
		47.1		34.0	
Ethyl alcohol	2903.8	2985.0			
		81.2			
Ethyl ether	2874.1	2947.4	2991.7		
		117.6			
Sulphur dioxide	2488.1	2512.0			
		23.9			

separate lines, or, in other words, to reveal the fine structure of the bands. It is probable that, except in the case of acetylene and ethylene, the individual lines of the bands lie so close together that it would be hopeless to separate them by any spectral apparatus now existing. The absorption curves represent the integrated effect of several lines

which are covered by the slit at a single setting. Such a curve, may be called the envelope of the band. By examining this envelope it may be stated in some cases of what branches a band is composed, especially when the band appears to be a doublet having P and R branches only.

The entire region from 3 to 4μ was not examined for each gas. The curves obtained with a prism[1] were used as a guide in selecting the region to be studied, but the exploratory runs were carried quite far beyond the indicated region, in order to be certain that the region of absorption was being completely covered.

Those compounds which are liquid at ordinary temperatures and pressures, were vaporized by drawing air from the room over the liquid in the bottom of a U-tube. One end of the U-tube was connected to the inlet tube of the absorption cell. The outlet tube of the cell was connected to the side tube of an aspirator; a jet of air from the compressed

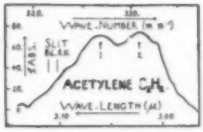

FIG. 1.

air line of the laboratory was blown through the aspirator. The air pressure in the cell and in the arm of the U-tube which was connected to it, was thus slightly reduced, causing the liquid to rise in that arm and fall in the other, thus drawing air from the room in bubbles, through the liquid, for a distance of one or two cm, and thereupon into the cell. The air was probably not saturated with the vapor, however varying the rate of bubbling, or varying the amount of liquid in the bottom of the tube within reasonable limits, had no marked effect upon the percentage of absorption. The liquid in the U-tube had to be replenished from time to time during the run, and this was troublesome. To avoid doing so, the rubber hose connections at the inlet and outlet of the cell were sometimes closed off with screw cocks. A small amount of vapor then diffused out of the cell during the observations but checks made at the close of the run on selected points of the absorptions band gave assurance that the diffusion was kept within permissable limits. It would have been better to seal glass stopcocks to the inlet and outlet tubes. When this is done, gas can be kept in a cell for a week or more without noticeable diffusion, as subsequent experience has shown.

Following are details regarding the work on the individual compounds and the results obtained:

Acetylene, C_2H_2, Fig. 1, cell length 1 cm: The gas was generated by dropping water on to calcium carbide and was then dried. It was passed through the cell continuously during the observations. The absorption curve suggests that the band is a doublet having *P* and *R* branches only. The wave-number difference between the maxima gives a datum regarding the moment of inertia of the acetylene molecule; it is equal to 41.1 cm^{-1}.

Ethylene, C_2H_4, Fig. 2*a*, cell length 1.2 cm: The gas was generated by adding water and ethylene dibromide to granulated zinc and then heating. It was passed through a tower containing sodium hydroxide and thereupon through a tower containing concentrated sulphuric acid. The gas flowed continuously during observations. The curve suggests that maximum No. 1 is a *P* branch, No. 2 a faint *Q* branch, and No. 3 an *R* branch of one band, and that maxima Nos. 4 and 5 are *P* and *R* branches of an adjacent band. The wave-number difference between maxima Nos. 4 and 5 is 42.6 cm^{-1}, nearly the same as for acetylene. Exact agreements in wave-number differences are not to be looked for. It is impossible to determine the positions of the absorption maxima with the full degree of accuracy which is intrinsically possible with a grating spectrometer, because of the breadth of the maxima. Moreover, when the maximum of an envelope is located by measuring the absorption produced by a number of lines which are covered by the slit at one setting, as in the present work, then the position of this maximum is in itself not an entirely definite thing. It depends slightly upon the positions chosen for setting the circle, even though these positions are taken so closely together that the slit images in successive positions overlap, as they do when settings are made at intervals of one minute of arc.

n-Butane, C_4H_{10}, Fig. 2*b*: The gas was obtained from the Carbide and Carbon Chemicals Co. in a cylinder. The manufacturers state that it has a purity of 98 per cent, the balance being iso-butane and propane. A small amount of gas was introduced into the cell, which was adjusted to 8 cm. in length, and then the inlet and outlet tubes were closed off. An exploratory run had shown that the absorption would be too high for favorable observation, even with a short cell, if it were completely filled with gas. Hence the cell was adjusted for a convenient length and the gas diluted with air. The absorption curve does not suggest an interpretation of the band or bands in terms of branches.

The wave-number difference between maxima Nos. 1 and 2 is about the same as that between Nos. 3 and 4, but this may have no significance. No. 4 is poorly defined and difficult to locate.

n-Hexane, C_6H_{14}, Fig. 2*c*, cell length about 5 mm: The liquid was obtained from the Research Laboratory of the Eastman Kodak Co. The vapor was drawn into the cell by inserting the liquid in a U-tube and drawing air over it. The inlet and outlet tubes were closed off during the run. The absorption curve suggests that maxima Nos. 2 and 3 are respectively *P* and *R* branches of a band. Maximum No. 1 is probably a distinct band.

n-Octane, C_8H_{18}, Fig. 2*d*, cell length 5 cm: The liquid, obtained from Eastman, was inserted into a U-tube and air drawn over it continuously during the run. Only one run was taken over this band at one minute intervals and this was not entirely completed at the time of taking it. When the omission was discovered, the grating had been removed and the spectrometer had been adjusted for work in another region of the spectrum. Hence, it was inconvenient to complete the curve. The observations terminate at about 3.37μ whereas they should have been carried to 3.34μ. An exploratory run, taken at five minute intervals, shows that the absorption falls off rapidly beyond 3.37μ, but failure to complete the one-minute run makes it impossible to locate the last maximum or indicate its height relatively to No. 2. Maxima Nos. 1 and 2 in octane appear to correspond to Nos. 1 and 2 in hexane. The wave-number differences between the two pairs are certainly about the same and are perhaps exactly equal. Maximum No. 1 in octane is difficult to locate on account of the irregularity of the curve in this region which may be due to accidental error. It should perhaps have been located further to the right.

Benzene, C_6H_6, Fig. 2*e*, cell length 4.5 cm: The liquid, labelled c.p., thiophenefree, obtained from the chemical stock room, was placed in a U-tube, and the vapor was drawn into the cell. The inlet and outlet tubes were closed off during the run. The absorption curve suggests a doublet having *P* and *R* branches only. Moreover, the band appears to be degraded toward short wave-lengths, a circumstance which is unusual in vibrational-rotational bands.

Toluene, $C_6H_5 \cdot CH_3$, Fig. 2*f*, cell length 9.5 cm, from the chemical stock room: The vapor was drawn into the cell continuously during the run, by drawing air over the liquid in a U-tube. The absorption curve suggests two adjacent bands, but their structure is not clear.

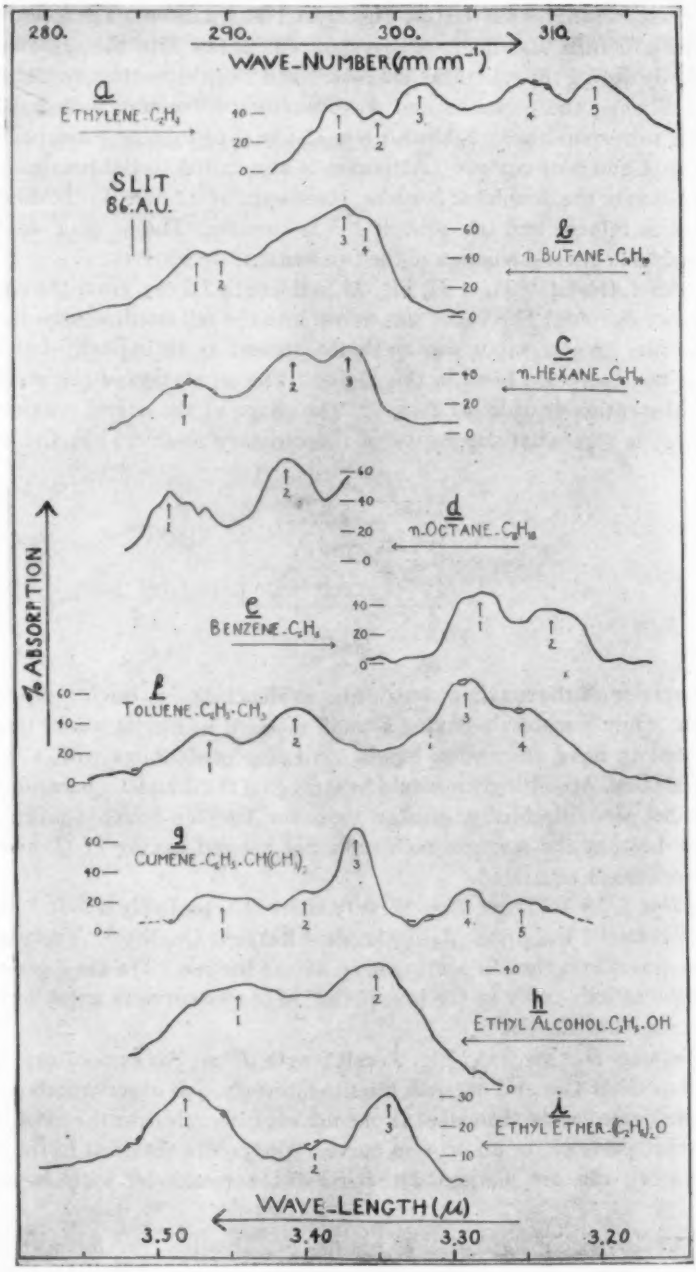
280.
290.
300.
310.
WAVE-NUMBER(m m⁻¹)
a
ETHYLENE-C₂H₄
SLIT
86.A.U.
b
n.BUTANE-C₄H₁₀
c
n.HEXANE-C₆H₁₄
d
n.OCTANE-C₈H₁₈
e
BENZENE-C₆H₆
f
TOLUENE-C₆H₅-CH₃
g
CUMENE-C₆H₅-CH(CH₃)₂
h
ETHYL ALCOHOL-C₂H₅-OH
i
ETHYL ETHER-(C₂H₅)₂O
% ABSORPTION
WAVE-LENGTH(μ)
3.50
3.40
3.30
3.20

FIG. 2.

Cumene, $C_6H_5 \cdot CH(CH_3)_2$, Fig. 2*g*, cell length 28 cm: The liquid was obtained from Eastman. The vapor was drawn into the cell continuously during the run. Maxima Nos. 1 and 2 correspond to Nos. 1 and 2 of toluene; the positions and wave-number differences both indicate this correspondence. Likewise Nos. 3 and 4 of toluene correspond to Nos. 4 and 5 of cumene. Attention is also called to the proximity in position of the doublet of benzene, considered as a whole, to the doublet 3–4, in toluene and the doublet 4–5 in cumene. The benzene doublet persists in general position in the two benzene derivatives.

Ethyl Alcohol, $C_2H_5 \cdot OH$, Fig. 2*h*, cell length 7.5 cm, from the chemical stock room: The vapor was drawn into the cell continuously during the run. Water vapor was no doubt present as an impurity but this has no absorption band in this region. The separation of the maxima of absorption is wide, 81.2 cm^{-1}. The shape of the curve, considered alone, is somewhat suggestive of the ordinary doublet, but the wide

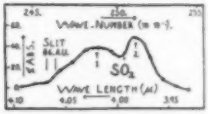

FIG. 3.

separation of the maxima contributes evidence against such a supposition. Only a molecule having a small moment of inertia would be expected to have absorption bands consisting of doublets with a wide separation. Accordingly it would be strange if the doublet separation for alcohol were decidedly greater than for simpler related gases. It may be that the maxima each represent a band having *P*, *Q*, and *R* branches not separated.

Ethyl Ether $(C_2H_5)O$, Fig. 2*i*, very short cell, probably about 3 mm: The material was from Mallinckrodt, "Reagent Quality." The vapor was drawn into the cell continuously during the run. The same general considerations apply to the interpretation of this curve as apply to the one for ethyl alcohol.

Sulphur Dioxide, SO_2, Fig. 3, cell length 2 cm: An exploratory run was made at two and one-half minute intervals, and observations were made immediately thereafter at one minute intervals over the most important parts of the absorption curve. The points obtained in the exploratory run are marked with circles, the remainder with crosses.

The band is apparently a doublet consisting of P and R branches. The wave-number difference between the maxima is 23.9, being less than the wave-number differences between the maxima in the bands of carbon dioxide[5] which are about 30 cm^{-1}.

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SWARTHMORE, PENNSYLVANIA.
AUGUST 1927.

[5] Barker, E. F., Astrophys. Journ., *55*, 5, p. 391; 1922.

ORGANIC MEDIA AS SPECTRAL FILTERS IN THE ULTRAVIOLET[1]

By Thos. M. Dahm

ABSTRACT

Aqueous solutions of organic media were examined by the extinction point method, using a geometrical series of concentrations, in a search for media having high gradation of absorption in the ultraviolet region.

Curves of log (concentration) against frequency ν of extinction point are shown for thirty-two compounds, grouped as to spectral region in which the curves have high slope. Five compounds had not been studied previously: gallic and tannic acids, aniline arsenate, arsanilic acid, and p-dichlorobenzene.

The quantity a, the slope of the curve of log i against ν, is shown to be the sole significant factor in determining gradation of absorption. Media having rectilinear log i curves are shown to have constant gradation of absorption of a degree proportional to the slope of the curve.

Curves of log b, log c, and log log $1/T$ are shown to have an invariant form, that of the curve of log i. It is shown that use of these curves locates directly the frequencies at which a is highest; leads to simple methods of testing Beer's Law, of determining low solubility, and of finding "true half breadth" of absorption lines; and permits partially graphical solution of other absorption problems. The relations between the curve of a mixture of two solutes and the curves of the components are developed.

The extinction point method is shown to have certain advantages over other methods because of the low value of transmittancy involved, and to be adequate for determination of a when a is high. A modification of it, involving use of a *constant* low transmittancy T, is suggested.

INTRODUCTORY

The limitations as to intensity and spectral purity of the ultraviolet radiant flux transmitted by the monochromatic illuminator suggest a search for spectral filters to be used with it,[2] or to replace it in experiments that can be carried on with a moderate irradiation of a large surface by a radiant flux covering a range of frequencies sharply limited at one or both ends, requirements of certain photochemical experiments. For photoelectric potential work, a filter must have so high a gradation of absorption as to transmit a given line strongly and cut off lines of higher frequency. Silver films, colloidal silver solutions, and very thin mica or ordinary glass transmit ultraviolet energy, but show small gradation of absorption.[3] Dyes that retain color at extreme

[1] Reference is made to this work by R. C. Williamson, Phys. Rev., *21*, p. 107; 1923, and by R. J. Piersol, Phys. Rev., *23*, p. 144; 1924. Partial reports on it appear in Phys. Rev., *26*, p. 285; 1925, Abstract No. 13, and in Phys. Rev., *27*, p. 246; 1926, Abstract No. 17.

[2] Millikan, R. A., Phys. Rev., *7*, p. 355; 1916. Use was made of an aesculin filter to eliminate stray radiant flux of wave-length below 4047A.

[3] Bur. Standards Tech. Paper 148, 1920, and Gibson, K, S., J. O. S. A. & R. S. I., *13*, p. 267; 1926, show data on solid media some of which show high gradation of absorption in the ultraviolet region of the spectrum.

dilution evidently have high gradation in the visible. Similar uncolored organic compounds should be examined as to this property, since but a small part of the data accumulated by chemists[4] using the Hartley extinction point method is presented in such form as to make gradation of absorption determinable.

In connection with a study of the voltage-frequency relation in the photoelectric effect of platinum an attempt was made to find suitable absorption media. While the very small photocurrents characteristic of platinum prevented a successful outcome for the photoelectric experiment, the search for spectral filters produced data that may prove useful and theoretical results that have a bearing on methods of obtaining and of presenting absorption data.[5]

APPARATUS AND METHOD

A rather old Cooper-Hewitt quartz mercury arc, run at 4 amp. current with 56 V across the lamp was used. It was enclosed by a wooden box with small ventilation and was always run for an hour before spectra were taken. The arc was very steady and the current when warmed up was always closely the same for 110 V across the lamp and built-in ballast resistance. This arc was somewhat weaker below 2400A than new arcs tested.

A Hilger constant deviation quartz monochromatic illuminator was used, with exit slit replaced by a camera. It was adjusted for collimation and minimum deviation at 2700A, and gave a spectrum two inches long from 4047A to 2302A. Ghosts, bracketting the lines with decreasing separation as collimation was approached, are attributed to the fact that the mirror had been coated on the back instead of the front. For long exposures, desirable with the extinction point method, the excessive power of 4047A and 3655A was reduced by focussing the unachromatized 2″ condensing lens at 2500A with a slightly enlarged image on the slit which had a length of 1/8″, covering the center of the lens with a 7/8″ disk, and limiting the area of the source with a 1/4″ diaphragm almost

[4] This field is discussed in Baly's Spectroscopy, p. 409, and in Kayser's Handbuch d. Spectroscopie, *3*, p. 154. A catalogue of substances examined is found in the 1916 report of the Brit. Assoc. Adv. Science, p. 131, with additions appearing in the 1920 Report.

[5] Report on Spectrophotometry, J. O. S. A. & R. S. I., *10*, p. 169; 1925. The terminology and notation of this report are adopted in this article. Exception is taken, however, to the estimate of the value of Hartley's method (p. 224). It will be shown that the method should give more precise results than has been believed, and that by it precise determination may be made of the quantity a, the slope of the curve of log i against frequency. This slope will be shown to be the the most important characteristic of a medium from the spectral filter standpoint.

in contact with the quartz tube of the arc. With this hollow conical pencil of rays, the photographs of spectrum lines between 3600A and 2200A were apparently of constant intensity over the whole length of the slit image, but outside these limits progressively more of the slit was within the umbra of the disk on the lens.

The solutions examined were placed in a tubular glass cell 50 mm long and about 30 mm in diameter with crystalline quartz ends totalling 9 mm in thickness. These plates were at first waxed on with resin-beeswax, but later clamped lightly with U-shaped brass strips faced with leather, making the cell easy to clean and reducing evaporation of volatile solutes. When solutions were changed the cell was rinsed at least once with about half its volume of the new solution.

Redistilled ethyl and methyl alcohols intended for use as solvents showed strong absorption, probably due to oxidation products which are difficult to remove completely.[6] Only distilled water was used as a solvent, as all the substances examined except triphenyl phosphate, gave complete absorption for some part of the spectrum, though some of them are supposed to be quite insoluble in water. Most of them were dissolved at boiling temperature and allowed to crystallize out on the undissolved portion for several days. Liquid solutes often gave turbid solutions on cooling but cleared up in time. A geometrical series of relative concentration 1 (usually saturated), 1/2, 1/4, etc. was prepared for each substance. These steps are short enough for adequate examination of any substance likely to prove useful as a spectral filter. The series was extended until complete absorption was evident in no part of the spectrum; frequently beyond a relative concentration of 1/(2048).

The spectra were taken on Seed 30 5×7″ plates cut into 2×5″ strips, and were developed in Metol-Hydrochinone. Slit width was so adjusted that a 10 sec unabsorbed exposure brought out the continuous spectrum very weakly elsewhere than immediately above the reversed line 2535A where it is very strong for a range of about 50A. Absorption spectra of three concentrations, each with a 10 sec and an 80 sec exposure time and two 10 sec unabsorbed spectra were taken on each plate. At first, the unabsorbed spectra were placed first and last, but later adjacent to the 80 sec spectra. Since it was found that in regions of high gradation spectra with 80 sec exposure were extended into the totally absorbed region but slightly beyond those with 10 sec exposure, a camera shutter timed with a watch was considered sufficiently accurate. Effects of

[6] The spectra of all weakly absorbing media are doubtful, since (See Sec. 7) small amounts of strongly absorbing impurities may distort the curves.

variation in radiant flux and of inaccurate timing are much smaller with low than with high transmittancy.[7]

The following substances were examined in aqueous solution: One inorganic salt—bichloride of mercury: Fourteen acyclic compounds—methyl, ethyl, and allyl alcohols; oxalic, acetic, citric, tartaric, citraconic, mesaconic, fumaric, maleic, crotonic, and aconitic acids; and thiocarbamide: Forty-two carbocyclic and heterocyclic compounds—phenol, hydrochinone, pyrogallol, and phloroglucin; benzoic, salicylic, phthalic, p-hydroxybenzoic, gallic, tannic, phenylacetic, and picric acids; aniline arsenate and arsanilic acid; p-dichlorobenzene, acetanilide, benzamide, triphenyl phosphate, heliotropin, diphenyl, phenanthrene; quinine sulphate and hydrochloride, strychnine sulphate, berberine and cryptopine hydrochlorides; aconitine, atropine, cinchonidine, cinchonine, cocaine, morphine, narcotine, and their hydrochlorides; thiophene; and 2:5 dimethyl pyrazine. Of the above substances, five had not previously been examined—gallic and tannic acids, aniline arsenate and arsanilic acid, and p-dichlorobenzene.

On each absorption spectrum the points were noted at which spectrum lines just failed to appear on 10 sec exposures while appearing very faintly on 80 sec exposures. The frequencies of these extinction points expressed in fresnels (1 fresnel $=10^{12}$ vibrations per sec) were plotted as abscissas. As ordinates, the ordinal numbers of the series of concentrations, counting the most concentrated as zero, were used as a scale, plotted downward. Since a geometrical series of concentrations of ratio 1/2 was used, this ordinate scale is in fact the logarithm of the relative concentration with 2 as a logarithmic base.[8]

[7] An attempt was planned to determine from the plates what concentration should be used to give T_{sol}, the transmittancy of the solution, a particular value at a given frequency. Points of equal density in 80 sec absorbed and 10 sec unabsorbed spectra would determine the frequency and concentration at which T_{sol} is 1/8, if the reciprocity law is nearly enough true for this ratio of exposure times. Determination of T_{sov}, transmittancy of the solvent, in a similar way would then determine T, transmittancy of the solute, at this point, since $T_{sol} = T \cdot T_{sov}$. However, variability of the Schwarzschild exponent p (See Ref. 16) probably invalidates this method. Had a sector photometer (See Refs. 12 and 13) been available, the method of Sec. 2 would have produced completely quantitative results.

[8] In the Hartley method extinction points expressed as "oscillation frequencies" ($1/\lambda$, λ in *mm*) are plotted as abscissas. The ordinates are either concentrations if length of cell is constant, or cell lengths if concentration is constant, or reciprocals of whichever one is varied. Baly and Desch (London Chem. Soc. Trans., *85*, p. 1029; 1904.) suggested the use of the logarithm of concentration (or of length of cell) as ordinate. They pointed out that from the nature of Beer's law concentration enters in such a way that it is the relative variations in concentration that count. It will be shown that, among other good reasons for using this form, it is especially useful in the study of gradation of absorption since the slope of the log c curve measures the gradation (See Sec. 3). Because of the nature of logarithms, the graph of

RESULTS

Table 1 lists substances the graphs of which are plotted in Figs. 1, 2, 3, and 4. With the exception of previously unexamined substances shown in Fig. 2, no substance is shown unless its graph is of high slope at some point. Intersections of the curves with the topmost line of the

TABLE 1. *List of substances the* $\log_2 c$ *graphs of which appear in* FIGS. 1–4 *with corresponding numbers.*

1. Mesaconic Acid	17. Phthalic Acid.
2. Thiocarbamide.	18. Cryptopine Hydrochloride.
3. Citraconic Acid.	19. Strychnine Sulphate.
4. Crotonic Acid.	20. p-Hydroxybenzoic Acid.
5. Bichloride of Mercury.	21. Phenol.
6. Citric Acid. (unsat.)	22. Benzoic Acid.
7. Tartaric Acid.	23. Benzamide.
8. Acetic Acid. (unsat.)	24. Acetanilide.
9. Heliotropin.	25. Cinchonidine Hydrochloride.
10. Quinine Hydrochloride.	26. Cinchonine Hydrochloride.
11. Quinine Sulphate.	27. Cinchonine.
12. Tannic Acid	28. Hydrochinone (acid solvent)
13. Arsanilic Acid.	29. Phenylacetic Acid.
14. Gallic Acid.	30. Atropine.
15. Aniline Arsenate.	31. Atropine Hydrochloride.
16. p-Dichlorobenzene.	32. Thiophene.

Excepting Nos. 6, 8, and 28, the first solution photographed was an aqueous solution saturated at 21°C in the case of each substance in this list. No. 6 begins with a solution of 25g of citric acid in 150g of water. No. 8 begins with a 2% solution. To retard oxidation, the solvent for No. 28 was modified by combining 1 part of saturated oxalic acid solution with 99 parts of water. The oxalic acid does not appreciably affect the curve because the series of concentrations was made by adding distilled water. The curve of No. 31 is drawn in part as a broken line to lessen confusion with other curves.

figure are extinction points for 50 mm thickness of aqueous solution saturated at 21°C, except as noted in the footnote of Table 1. Because of the relation of the ordinate scale to the ratio of the series of concentrations, all observed points are on horizontal coordinate lines. The points

log c against ν has a form quite independent of the units in which concentration is expressed. The use of relative rather than actual concentration brings the starting points of all curves to the top of the figure. It also obviates the necessity of adding several ordinate scales when a number of curves appear in the same figure. Furthermore, it enables one to graph very slightly soluble substances of which no more is known that that the initial solution is saturated.

The use of 2 as a logarithmic base is convenient when the ratio of concentrations is 1/2. The scale may readily be changed to a common logarithm scale, since an ordinate difference of 1 on the $\log_2 c$ scale is equal to an ordinate difference of .30103 on a $\log_{10} c$ scale.

are connected by straight lines unless the slope is obviously changing rapidly. Abscissas of maxima and minima are quite accurate because, as shown in Sec. 1, the extinction point method magnifies the effect of small relative variations in i, the specific transmissive exponent (absorption coefficient). To locate the ordinates precisely requires shorter steps in concentration than were used, although the intensity of lines near these points in the spectrum in which they almost fail to appear does indicate in which third of the vertical interval between coordinate lines the curve should be drawn.[9]

It will be noted that the curves of Fig. 1 have rather long straight portions. Examination of the photographs of the geometrical series of concentrations shows that there is a constant difference between the

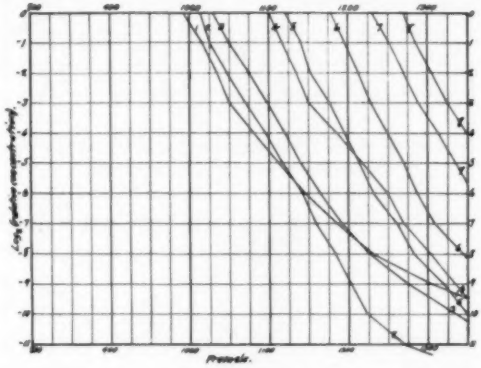

FIG. 1. *Log c graphs showing small gradation of absorption extended over a wide range of frequencies.*

frequencies of extinction points of the spectra of successively less strongly absorbing solutions, as should be expected from the linear nature of the curves. Furthermore, *the gradation of absorption is the same in every spectrum;* that is, the range of frequencies within which the transmission falls from practically that of the solvent to practically zero is of the same length for each spectrum. As a consequence, the medium may be used as a spectral filter limiting the length of the spectrum transmitted equally well at all frequencies within the range over which

[9] The relationship between these curves of log c against ν and the original spectra may be clarified by pointing out that if the spectra, magnified to the proper frequency scale, were each superposed on the horizontal coordinate line corresponding to the concentration with which the spectrum had been obtained, then every spectrum would end on the curve. The region above and to the right of the curve is the totally absorbed region.

the curve is linear by choosing proper concentrations. Another important property appears in the observation that the steeper the curve, the shorter the frequency range within which transmittancy falls to zero.[10]

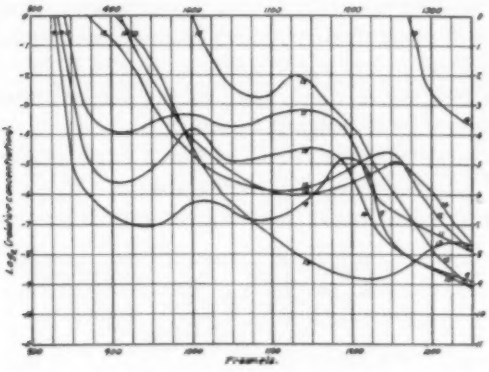

FIG. 2. *Log$_{10}$c graphs showing high gradation near 850f. Nos. 12–16 are graphs of previously unexamined compounds.*

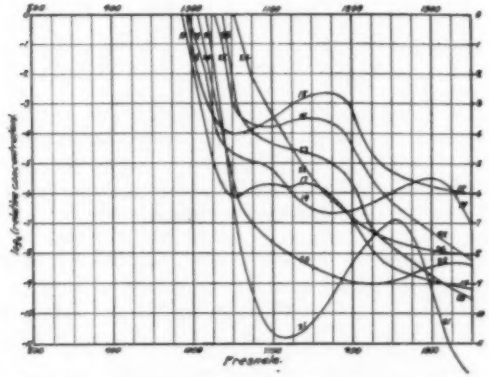

FIG. 3. *Log$_{10}$c graphs showing high gradation near 1000f.*

Fig. 1 shows substances with nearly linear curves that may be used to limit the spectrum to low frequencies fairly sharply at any point above $1000f$ (below 3000A). Figs. 2, 3, and 4 show substances with curves of

[10] These empirical facts will be shown in Secs. 3 and 6 to be logical consequences of Beer's law of absorption and of the fact that on the side of a broad deep absorption band the curve of specific transmissive exponent against frequency may often be closely approximated by an exponential curve.

very high slope in narrow spectral regions, arranged for visual comparison of slope. Fig. 2 covers a narrow region about $850f$; Fig. 3, a broader one mostly above $1000f$; Fig. 4, a narrow one above $1200f$, and another about $1300f$, for which curve 21 also applies.

It will be shown in Secs. 6 and 8 that the curves may be used to predict the values of T (transmittancy of the solute, or fraction of the total energy transmitted by the solute) at other frequencies than that for which T has been adjusted to some desired value by a proper choice of concentration and of length of cell. The process is as follows: Having decided that T shall have a particular value at a certain frequency, find the point where the curve passes through that frequency. From this point drop vertically one unit on the $\log_2 c$ scale and then go

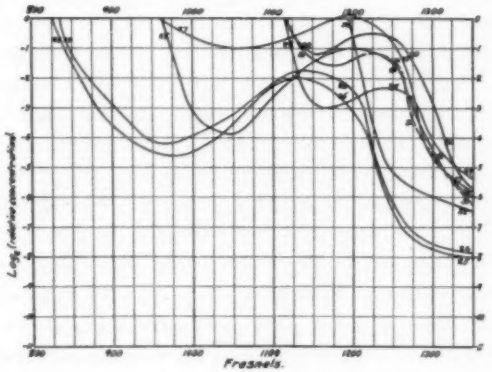

FIG. 4. *$\log_2 c$ graphs showing high gradation near $1200f$ and $1300f$.*

horizontally to the curve at which will be found the frequency for which the transmittancy will be T^2. If, instead of dropping one unit, one drops 2, 3, etc. units, the transmittancy at the frequency found by going to the curve is T^4, T^8, etc. If, instead of dropping, one rises from the original point 1, 2, 3, etc. units, the transmittancies found by going to the curve horizontally from the points reached by the respective upward steps are $T^{1/2}$, $T^{1/4}$, $T^{1/8}$, etc. (On a $\log_{10} c$ scale, a drop of one unit locates the frequency at which transmittancy becomes T^{10}. In other words, the exponent of T is the antilogarithm of the difference of logarithms involved.) While allowance must be made in practice for the fact that $T_{sol} = T \cdot T_{sov}$, the transmittancy of the solution is the product of the transmittancies of solute and solvent, it will be shown in Sec. 8 that curves taken by the extinction point method which apparently

ignores T_{sov} can, nevertheless, be used for this prediction of values of T so long as T_{sov} does not vary rapidly.

In view of the facts just stated, it is evident that in the spectral regions for which no curve of very high slope has been found one of the substances shown in Fig. 1 may be used to limit the spectrum at a particular spectrum line when the conditions of the experiment permit use of a low value of T for this line. For example, suppose that the concentration of citraconic acid, curve 3, is so adjusted that $T=1/2$ at $1050f$. Then $T=(1/2)^2$ at $1075f$ and $T=(1/2)^4$ at $1098f$. But if $T=1/8$ at $1050f$, $T=(1/8)^2$ at $1075f$ and $T=(1/8)^4$ at $1098f$. For the region from $1020f$ to $1120f$, No. 2 is probably best; from $1120f$ to $1230f$, No. 5; from $1180f$ to $1300f$, No. 6; and above $1300f$, No. 7, though the initial concentration of No. 6 is so high as to suggest possible failure of Beer's law.

While for most of the substances in Fig. 1, $\Delta\nu$ corresponding to a change from T to T^2 is about $25f$, it is but $5f$ for No. 9 between $829f$ and $840f$, $5f$ for No. 21 between $1018f$ and $1048f$, and but slightly more than this for several other compounds in these two regions. $\Delta\nu$ for a change from T to T^2 is $8f$ for No. 29 at $1115f$, $7f$ for No. 32 at $1195f$ increasing to $9f$ at $1220f$, $10f$ for No. 26 at $1221f$, $7f$ for No. 31 at $1263f$, $9f$ for No. 27 at $1270f$, $7f$ for No. 16 at $1283f$, $11f$ for No. 21 from $1286f$ to $1320f$, and $10f$ for No. 30 at $1303f$. The value of $\Delta\nu$, corresponding to so small a change in transmittancy as a change from T to T^2, is used here for the purpose of indicating at what points the curves are steepest. Inspection of the graphs shows that many of them continue steep for a sufficient vertical interval to make it possible to consider much larger changes in T without involving such large values of $\Delta\nu$ as to exceed greatly the distances between spectrum lines that are to be found in such spectra as that of the mercury arc. When the lines are not too close together it is quite possible to give T a value of .50 at one line and practically zero at the next. This is true especially for such long extended steep graphs as Nos. 9 and 21, as may be seen by noting that for them a $\Delta\nu$ of $10f$ changes T to T^4 and a $\Delta\nu$ of $15f$ changes T to T^8. Even when the curve is steep only for a short distance, it may be useful if a strong spectrum line happens to occur at the low frequency end of the steep portion and if the next strong line is at some distance without too many weak lines between.

Absorption bands are usually shifted toward the red by the addition of methyl or ethyl groups, and by other additions to the weight of the molecule. Forming the hydrochloride of an alkaloid may steepen its

curve and shift it toward the red. Brode[11] shows the effects of solvents on band position and presents qualitative data on T_{nov} for many organic solvents. It must be borne in mind that the use of solvents which show great variation of transmission within short frequency ranges would distort curves obtained by the extinction point method. (See Sec. 8.)

It is probably unsafe to assume that the curves here presented will be exactly reproduced by other samples of these organic compounds, at least insofar as the upper parts of the curves are concerned, because, as shown in Sec. 7, even small quantities of strongly absorbing impurities may greatly distort the curves in the less strongly absorbing regions. Such distortion is, of course, independent of the method used to obtain the data.

The spectra of highest concentration of media Nos. 16, 29, and 32 all show extremely high gradation, indicating that their curves continue steep beyond the region examined. These, and others the curves of which for an aqueous solution begin at high frequency, need examination in other solvents.

The permanence of these filters should be studied. A photoelectric experiment on platinum with a solution of phenol limiting the spectrum at 2378A showed no change in photocurrent during some hours of irradiation by the mercury arc. But thiophene, limiting the spectrum at at 2534A, gradually reduced the current by one third during a series of intermittent exposures totalling two hours. No change in properties occurred when the thiophene was not exposed to radiation from the arc. Its spectrum taken after the experiment showed decreased transmission near the extinction point.

THEORETICAL

1. GENERAL CONSIDERATIONS

Except in the case of very concentrated solutions the validity of Beer's law is generally assumed. This law states that

$$T = e^{-ibc}; \qquad (1)$$

T, the transmittancy or fraction of the total energy transmitted by the solute, is equal to the negative exponential function, the exponent being the product of specific transmissive exponent (absorption coefficient) i, length of cell b, and concentration c, variations in all three of which are interchangeable. Of the four quantities in Eq. (1) only i is intrinsically a function of frequency, so that determination of the ab-

[11] Brode, W. R., Jour. Phys. Chem., *30*, p. 56; 1926.

sorbing properties of a substance is essentially the problem of determining the manner in which i varies with the frequency ν.

The sector photometer method used by Howe[12] and by the Bureau of Standards[13] holds b and c fixed and determines the way in which T varies with ν. While this method determines the transmission of a particular filter, even when Beer's law does not hold, it cannot give accurate information as to the variations in i in those spectral regions where T is high. The way in which relative variations or percentage changes in T depend on the relative variations in i is best brought out by putting $i=f(\nu)$ and finding $d(\log T)/d\nu$ and $d(\log i)/d\nu$, the logarithmic derivatives or "percentage rates of change." The ratio of $d(\log T)/d\nu$ to $d(\log i)/d\nu$ is found to be $-ibc$. When $T=.3679$ (e^{-1}) the percentage rate of change of T is equal to that of i. When T is high (ibc small) very large relative variations in i have little influence on T, as even casual inspection of a series of absorption spectra shows, whereas in the regions of low T small relative variations in i produce very large relative variations in T.[14]

The extinction point method attempts to hold T fixed at a very low value and varies either b or c reciprocally to the variations in i. Formerly only sources furnishing line spectra were available, so that extinction meant very different values of T for lines of different strength, the basis of Howe's objection[12] to the use of such sources. However extinction means so very low a value of T that but very small relative variations in the values of i, or of ibc, correspond to these large variations in T from line to line. In other words, when T is sufficiently low even

[12] Howe, H. E., Phys. Rev., *8*, p. 674; 1916.

[13] Bur. Standards Sci. Paper 440; 1922.

[14] The value of $d(\log T)/d\nu\left[=(1/T)dT/d\nu\right]$ is $-f'(\nu)bc$. Its maximum or minimum absolute [numerical] values occur at the points of inflection of the curve of i against ν according as $f'(\nu)$ and $f'''(\nu)$ are of opposite or of the same sign. This derivative is obviously zero at the centers of absorption and transmission bands and at horizontal points of inflection, but elsewhere than at these centers its value may be increased by increasing b or c. Now precision in locating points of equal density on absorbed and unabsorbed spectra obtained with the sector photometer (neglecting effects due to variation in dispersion) does not depend on $dT/d\nu$, but on $d(\log T)/d\nu$. As T approaches zero, $dT/d\nu$ necessarily becomes small; yet photographs taken with low T, but with exposure time sufficient to produce contrast, show high gradation of blackening. It follows that b or c should be made large, thus reducing transmittancy, if one is to locate the points of equal density accurately. It thus appears that in those parts of a curve of log i against ν that are obtained from sector photometer data involving high T the points may be greatly displaced on the log i scale by a small percentage of error in the determination of T, and on the ν scale by inaccuracy in locating the points of equal density. How far one may go in reducing T depends largely on how much stray radiation of unabsorbed frequencies is present.

rough estimates of the relative variations in T give quite accurate knowledge of the relative variations in i. Consequently, it is by no means necessary to discard either the extinction point method or the use of line sources in order to obtain satisfactory results in the study of media that have high enough gradation to be used as spectral filters.[15] Since the use of low transmittancy emphasizes very small variations in i such as are found near maxima or minima of i, it follows that the centers of absorption and transmission bands may be located most accurately by the extinction point method if the medium is irradiated by a source having a continuous spectrum and if long exposures are made.

2. SUGGESTED MODIFICATION OF THE EXTINCTION POINT METHOD

It is not possible to compute from data taken by the extinction point method the value of c that should be used to give T a particular value at a given frequency because extinction means an undetermined value of T. This serious defect may be removed without losing the advantages of the Hartley method by finding the points of equal density in spectra of a series of concentrations and unabsorbed comparison spectra taken with a sector photometer, the sector being interposed only in the beam through the solvent and having a *small fixed* opening. The indeterminate and variable small value of T in the extinction point method would be replaced by a known constant small value.

As does also the usual sector photometer method, this suggested procedure assumes the validity of Howe's reciprocity law (See Ref. 12) which may be stated as follows: If two beams of unequal radiant intensity are simultaneously photographed with equal durations of exposure on adjacent portions of a plate, the radiant flux of the stronger being reduced by a rotating sector to an average flux equal to that of the weaker, equal densities will result. Should this conclusion not be valid, the actual values of i will be in doubt, but the relative values will be accurately found, unless the defect in this special reciprocity law should turn out to be a function of frequency, a result scarcely to be expected. Certainly, the law cannot hold for a very slowly rotating sector, since the Schwarzschild relation would hold if but one

[15] This statement is experimentally confirmed by the fact that the groups of log c curves in Figs. 1–4 show (at least in long-extended steep portions and when long exposures are used) no evidence of the warping that one might expect persistence of strong lines to produce. Investigation of broad shallow bands and of very narrow bands should, however, be carried out with a continuous spectrum, Howe's criticisms of line sources being valid in these cases.

turn occurred during exposure; that is, equal densities result if $I_1 t_1^p = I_2 t_2^p$, the exponent p being, however, subject to such variations as those indicated by Harrison and Hesthal.[16] But a rapidly rotating sector should approximate in results the oscillating screens used by Harrison,[17] which may also be used in the proposed constant T method.[18]

3. THE GRADATION CONSTANT a.

It has been pointed out that many of the absorption spectra examined extend the position of the extinction point in an arithmetical progression of frequencies when a geometrical progression of decreasing concentrations has been used, and that the gradation of absorption is practically the same in each spectrum of the series. The curves of log c against ν shown in Figs. 1–4 are over rather long ranges of frequency straight lines of slope $-a$, where a is defined by the equation

$$a = -d(\log c)/d\nu. \tag{2}$$

Since the spectra were taken with a quartz mercury arc as the source of radiant energy, extinction means a very variable but extremely small value of T. From the discussion of Sec. 1, it is seen that since ibc is large at extinction it is also practically constant, in spite of the variations of T. The method of Sec. 2 would make it strictly constant. If ibc and b are constant,

$$a = -d(\log c)/d\nu = d(\log i)/d\nu, \tag{3}$$

(a true relation also when a is variable) and i approximates on the side of a broad deep absorption band the integral relation

$$i = i_1 e^{a(\nu - \nu_1)}, \tag{4}$$

i and i_1 being the specific transmissive exponents at ν and ν_1, respectively, and a a constant that may be called the *gradation constant*.

For any fixed values of b and c, and at all frequencies within the range over which i actually fits the law of Eq. (4), T conforms to the following equivalent relations:

$$T = e^{-i_1 bc e^{a(\nu - \nu_1)}}, \quad dT/d\nu = -aibcT, \quad d(\log T)/d\nu = -aibc, \tag{5}$$
$$\text{and} \quad d(\log \log 1/T)/d\nu = a.$$

[16] Harrison and Hesthal, J. O. S. A. & R. S. I., *8*, p. 471, 1924.

[17] Harrison, G. R., Phys. Rev., *24*, p. 466; 1924.

[18] Bur. Standards Sci. Paper 440; 1922, discusses this law (Howe's) and gives experimental confirmation of it.

The constant a not only relates to each other the extinction points or other particular points of the spectra of different concentrations, but also serves as a measure of the changes in transmittancy within a single spectrum.[19]

Equality of gradation in the spectra of different concentrations will be shown in Sec. 6 to be a consequence of the linear nature of the log c curves. In practice, if the graph of log c against ν is a straight line over any considerable range of frequencies, the medium may be used as a spectral filter equally well at any spectrum line in this range by proper choice of concentration.

Since the value of a controls the rapidity with which the spectrum falls to zero, *the magnitude of the gradation constant a is a criterion of the usefulness of the medium as a spectral filter.*

4. INVARIANT CURVES

Eq. (1) may be put in the linear form

$$\log i = \log \log 1/T - \log b - \log c. \tag{6}$$

It follows from the linear form of Eq. (6) that if any two of the three quantities on the right hand side of the equation are held fixed the curve of the remaining one will have the *form* of the curve of log i, except for inversion if either b or c is the variable. The consequences of this fact are developed in the next two sections. The invariant nature (at a given frequency) of the right side of Eq. (6) is made use of to obtain Eqs. (7)–(14).

5. USES OF LOG LOG $1/T$ CURVES

If the data resulting from the variable T (sector photometer) method of study are plotted in the form of log log $1/T$ against ν, the curves (being equivalent in form to log i curves or to inverted log c curves) will show by their slopes at what frequencies a substance is best as a spectral filter.[20]

[19] The last of Eqs. (5) defines a also for non-linear log log $1/T$ curves; the third shows that the slope of the log T curve, with a constant, increases with decreasing T (and vice versa) from the value a at $T = .37$; from the second it may be shown that the slope of the T curve, with a constant, has a maximum absolute value equal to $.37a$ occurring at the point where $T = .37$.

[20] Although the graph of T(or T_{sol}) against ν should accompany every spectral filter, this form of graph is scarcely adequate for a study of substances with a view to use as spectral filters, since it conceals possible high values of a in regions of high T, gives no information about the totally absorbed regions, and does not show whether such values of b and c have been chosen as will cut off the spectrum at the frequency where gradation is highest. The graph of log T emphasizes absorption bands only when T is very low at their centers, as may be

If failure of Beer's law is suspected, a test may be made by repeating the experiment with a new value of concentration c_1, plotting the data in the form of a curve of log log $1/T_1$, and attempting to superpose the two curves by a vertical shift of amount computed from the relation

$$\log \log 1/T - \log \log 1/T_1 = \log c/c_1. \tag{7}$$

(A change in b will not test the law, since no change in the nature of the solution is then involved.) A relation similar to Eq. (7) may be used to find the values of log log $1/T$ that follow changes in b and c, assuming Beer's law.

In a similar way, solubility may be determined by finding the shift necessary to superpose the curve of a saturated solution on that of a nearly saturated one of known concentration.

The log log $1/T$ curve is also useful in finding the "true half breadth" of an absorption line, discussed by Harrison and Slater.[21]

6. USES OF LOG c CURVES

As indicated in Sec. 3, log c curves obtained either by the extinction point method or by the constant T method proposed in Sec. 2 will show by their slopes at what frequency the medium has the sharpest gradation of absorption. Also, if one uses the constant T method to obtain a second log c curve corresponding to a different value of T (produced by a different sector opening), a test of Beer's law may be made in the same way as with the log log $1/T$ curves by the use of Eq. (7). Low solubilities may be determined by obtaining two log c curves the initial points of which correspond respectively to a saturated and to a nearly saturated solution with a known value of c.[22]

A log c curve obtained by the proposed constant T method may be used to solve practical problems of which the following three may be mentioned:

a. Find what concentration c' should be used to change T to the value T_1 at ν_1. Find what value T_2 at ν_2 will have with this concentration c'.

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seen from the dependence on T of the slope of the log T curve (Ref. 19), and has otherwise the same faults as the graph of T. If a substance has long-extended high gradation complete data will not be obtained with one pair of values of b and c.

[21] Harrison and Slater, Phys. Rev., *26*, p. 176; 1925, and Slater, J. C., Phys. Rev., *25*, p. 783; 1925. Abstract No. 17, Phys. Rev., *27*, p. 246; 1926, covers the application to this problem of the invariant form of the log log $1/T$ curve.

[22] Unfortunately, the author did not realize the possibility of this method in time to determine by it the concentrations used in obtaining his data.

Using the invariant property of Eq. (6), we obtain

$$\log c' = \log c_1 + \log\log 1/T_1 - \log\log 1/T \tag{8}$$

and

$$\log\log 1/T_2 = \log\log 1/T + \log c' - \log c_2 \tag{9}$$

where $\log c_1$ and $\log c_2$ are read off the $\log c$ curve at ν_1 and ν_2, respectively. Instead of computing an extensive series of values of $\log\log 1/T_2$ by Eq. (9), one might use a rectangular transparent grid shifted vertically by an amount $(\log c' + \log\log 1/T)$ in accordance with the relation

$$-\log\log 1/T_2 = \log c - (\log c' + \log\log 1/T), \tag{10}$$

since the $\log c$ curve becomes an inverted $\log\log 1/T_2$ curve when so shifted.

b. Having found what concentration c' should be used to change T to the value T_1 at ν_1, find the frequency range $\Delta\nu = \nu_1 - \nu_2$ within which transmittancy falls from the value T_1 to the value T_1/p.

The value of ν_2 is found by locating on the $\log c$ graph the frequency at which $\log c_2$ has the value

$$\log c_2 = \log c_1 + \log\log 1/T_1 - \log\log p/T_1, \tag{11}$$

and the range within which T_1 falls to a value $1/p$ as great is $\nu_1 - \nu_2$.

Putting Eq. (11) in the form

$$\log c_1 - \log c_2 = \log c_1/c_2 = \log\log p/T_1 - \log\log 1/T_1, \tag{12}$$

it is seen that the left hand side is an ordinate difference of amount computed from the right hand side. In the a constant case, since the ordinate difference is the product of slope by abscissa difference, it follows that

$$\Delta\nu = (1/a)(\log\log p/T_1 - \log\log 1/T_1). \tag{13}$$

Since $\Delta\nu$ remains constant when a is constant and since $\Delta\nu$ is inversely proportional to a, this equation confirms the conclusions reached by observation as to constancy of gradation in spectra giving linear $\log c$ curves and as to increase of gradation with increase of slope.

From Eq. (12) it is seen that $\Delta\nu$ may be determined graphically for each of a series of spectrum lines by locating these lines on the curve of $\log c$ against ν, dropping vertically from each of them by the amount calculated from the right hand side of Eq. (12), and measuring horizontally to the curve. The slope of the curve in the a constant case is replaced by the slope of the secant of the curve when a is not constant, so that transmittancies at points between ν_1 and ν_2 are smaller or greater than in the a constant case according as the $\log c$ curve is concave upward or downward.

Since the operation just described involves only the ratio of concentrations and does not involve the value of T with which the data were obtained, it is applicable to log c curves obtained by the extinction point method even when the initial concentration is unknown.

c. Find the frequency range within which transmittancy falls from T_1 to T_1^n, n being any positive number.

Replacing T_1/p in Eq. (12) by T_1^n, we have

$$\log c_1 - \log c_2 = \log n, \tag{14}$$

from which $\Delta\nu$ is determined graphically as in the preceding problem; that is, by dropping a distance log n and measuring horizontally.[23] This process is the one suggested previously as a means of studying the curves of Figs. 1–4, since $\log_2 n$ has the values 1, 2, 3, etc. for $n = 2, 4, 8$, etc.

A table of values of the function on the right hand side of Eq. (12) was prepared to facilitate use of log c curves. Study of recurrence of certain numbers in it led to Eq. (14) which is so easy to apply that this table is omitted. Since it is sometimes convenient to consider step-wise variations in T rather than variations involving powers of T, Table 2 is included. This table is a series of values of the function $[\log_{10}\log_{10} 1/.125 - \log_{10}\log_{10} 1/T]$ which determines in a manner similar to Eq. (12) the values of the vertical drop, $\log_{10} c_1/c_2$, that must be made from any point on a $\log_{10} c$ (or rise from a $\log_{10}\log_{10} 1/T$) curve in order to find by horizontal measurement the frequency range within which T drops from any of the values of T in the table to the value .125. Inspection of this table shows that the successive differences in values of $\log_{10} c_1/c_2$ (by means of which are found the values of $\Delta\nu$ corresponding to the successive differences in T) are very large when T is large and have a minimum at $T = .37$. (See last statement, Ref. 19)

7. MIXED SOLUTES

If three solutions be made up, the first containing a concentration c_1 of solute no. 1, the second qc_1 of solute no. 2, and the third c_1 and qc_1, respectively, of the two solutes (which must not react chemically), the transmittancies of the three solutes in cells of length b are

$$T_1 = \epsilon^{-i_1 b c_1}, \quad T_2 = \epsilon^{-q i_2 b c_1}, \quad \text{and} \quad T_3 = \epsilon^{-(i_1 + q i_2) b c_1}. \tag{15}$$

The slopes of the three log log $1/T$ curves may be shown to be

$$a_1 = i_1'/i_1, \quad a_2 = i_2'/i_2, \quad \text{and} \quad a_3 = (a_1 + a_2 \cdot q i_2/i_1)/(1 + q i_2/i_1). \tag{16}$$

[23] Eq. (14) recalls the fact seen from Eq.(1), that if c_1 be changed to nc_1, T_1 will change to T_1^n for any positive value of n. It follows also that the frequency range within which, with concentration c_1, T_1 changes to T_1/p is the same range as that within which, with concentration nc_1, T_1^n changes to $(T_1/p)^n$. Or, the range for the change T_1 to T_1^n with c_1 equals that for the change T_1^n to T_1^{2n} with nc_1.

TABLE 2. *Values of vertical intercepts corresponding to changes in transmittancy from the value T to the value .125.*

T	$\log_{10} c_1/c_2$	T	$\log_{10} c_1/c_2$	T	$\log_{10} c_1/c_2$
.975	1.91454	.650	.68369	.325	.26721
.950	1.60789	.625	.64585−	.300	.23733
.925	1.42607	.600	.60967	.275	.20703
.900	1.29527	.575	.57492	.250	.17609
.875	1.19236	.550	.54136	.225	.14428
.850	1.10704	.525	.50882	.200	.11127
.825	1.03381	.500	.47712	.175	.07666
.800	.96936	.475	.44612	.150	.03985+
.775	.91159	.450	.41567	.125	.00000
.750	.85903	.425	.38564	.100	−.04427
.725	.81065+	.400	.35591	.075	−.09540
.700	.76567	.375	.32635+	.050	−.15856
.675	.72351	.350	.29683	.025	−.24895+

The numbers entered in the $\log_{10} c_1/c_1$ column are values of the function $[\log_{10}\log_{10} 1/.125 - \log_{10}\log_{10} 1/T]$ computed for the values of T appearing in the T column. [Cf. Eq (12).]

If a vertical drop of amount opposite T is made from any point of a $\log_{10} c$ curve, the horizontal distance to the curve measures the frequency range within which transmittancy changes from the value T to the value .125. To change from any value of T to another in the table, subtract the corresponding numbers. To change from T to a value $(.125)^n$, add $\log_{10} n$ to the number opposite T. If a $\log_e c$ curve is used, each number in the table must be multiplied by 2.3026 and $\log_e n$ must be used. If a $\log_2 c$ curve is used, each number must be multiplied by 3.3219, or divided by .30103, and $\log_2 n$ must be used.

a_3 is the weighted mean of a_1 and a_2. The combination curve, $\log\log 1/T_3$ lies above both component curves. Its greatest possible distance above the higher of the component curves is log 2 occurring where the component curves cross. At this point, the slope of the combination curve is the arithmetic mean of the slopes of the component curves. Since the weighting factor qi_2/i_1 is the antilogarithm of the difference in ordinates of the component curves, the combination curve must approach the upper component curve both in position and slope as the ordinate difference between the component curves increases. Except for inversion, this discussion also applies to $\log c$ curves, since the series of concentrations for the combined solute maintains the ratio q of the components.

If solute no. 1, of steep $\log c$ curve, cannot be used as a spectral filter at ν because of a transmission band at higher frequency, it should be combined with solute no. 2, the curve of which is fairly steep in a frequency range overlapping the centers of the absorption and transmission bands of solute no. 1. Such adjustment of qc_1 should be made that the curves intersect to the right of the center of the absorption

band but as near to it as is consistent with the requirement of a large ordinate difference at ν when the curve of solute no. 2 is not steep at that point.[24]

8. CORRECT VALUES OF a FROM EXTINCTION POINT CURVES

Applying the analysis of Sec. 7 to a solution, a mixture of two absorbing media, it is seen that in regions of low T the log log $1/T_{sol}$ curve will not differ greatly from the log log $1/T$ curve, while in regions of high T it may resemble the log log $1/T_{sov}$ curve. But a log c curve of data taken with T_{sol} constant lies everywhere only slightly below (below because of inversion) a log c curve, T constant, if T_{sov} is high and if the transmittancy used in taking the data is small, as it certainly is in the extinction point method. If T_{sov} decreases gradually with changing frequency, the interval between the log c curves of a solution and of the solute only will gradually increase. It follows that the extinction point method without correction for T_{sov} gives substantially accurate values of the slope of the log c curve, T constant, if T_{sov} does not change rapidly. Certainly, at a given frequency the relative values of a for two solutes may be accurately determined if the same solvent and length of cell are used to obtain the data.[25]

My sincere thanks are due to Professor Mendenhall for the use of the facilities of the Physics Department of the University of Wisconsin; to him and other members of the staff for advice and assistance; and to Professor Mathews and others of the Department of Chemistry, who supplied most of the compounds examined. Many of them were found in their collection of organic compounds, but others had to be made under their supervision.

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[24] The discussion of mixed solutes applies also if solutes 1 and 2 are placed in series instead of being mixed. It also applies as well to the determination of thickness of solid spectral filters to be used in combination.

[25] When it is preferable to use common logarithms and to determine the constant k, the specific transmissive index, a complete new set of equations, except for those given below, may be written down without numerical factors by substituting each of the quantities in the upper row for the one beneath.

$$10\ k\ k_1\ k_2\ k'\ k_1'\ k_2'\ F(\nu)\ F'(\nu)\ A\ A_1\ A_2\ A_3$$
$$e\ i\ i_1\ i_2\ i'\ i_1'\ i_2'\ f(\nu)\ f'(\nu)\ a\ a_1\ a_2\ a_3$$

10 is substituted for e both as a logarithmic base and when it appears explicitly. The exceptions are Eqs (5) and (16) which are replaced by

$$T=10^{-kbc\cdot 10^{A(\nu-\nu_1)}},\quad dT/d\nu=-(2.303)^2Akbc\,T, \tag{5a}$$
$$d(\log_{10}T)/d\nu=-2.303\,Akbc,\quad \text{and } d(\log_{10}\log_{10}1/T)/d\nu=A.$$
$$2.303A_1=k_1'/k_1,\ 2.303A_2=k_2'/k_2,\ \text{and } A_3=(A_1+A_2\cdot qk_2/k_1)/(1+qk_2/k_1). \tag{16a}$$

A is so chosen that $A/a=k/i$.

INSTRUMENT SECTION

A RADIATION METHOD OF MEASURING STRAIN IN GLASS

By C. E. Mendenhall, L. R. Ingersoll, and N. H. Johnson

The polarization method of testing for strain in glass has been known since the days of Brewster,[1] or for over a century. When the specimen is viewed between crossed nicols, the birefringence due to strain causes a "depolarizing" action—i. e., renders the plane polarized light elliptical—which lights up the field locally, giving both the location and an estimate of the magnitude of the strain. This method has been in use in glass factories for some time and has latterly been ingeniously applied by Coker[2] and others to the measurement of stresses in bridge models, etc., constructed of transparent materials.

It is obvious, however, that opaque glasses cannot be tested in this way. But many specimens, while almost opaque in the visible spectrum, will nevertheless transmit enough of the short infrared[3] for purposes of measurement: this is particularly true of glasses which scatter or diffuse the light. Accordingly if a radiation method can be used, with the aid of a suitable thermopile-galvanometer arrangement, it may be possible, not only to make measurements on ordinary transparent glasses, but also to test for strain in specimens which could not be worked with at all by visual means.[4]

METHOD

Optical System. As a source of energy a "pointolite" lamp is employed, the total radiation being used. No attempt is made at dispersion so all wavelengths from the ultraviolet to about $\lambda = 2.5\mu$ are present (this limit being set by the absorption of glass and calcite), but because of the form of the energy curve, transmission of the specimen, etc., the effective wavelength may be set at about 1μ. The light is focussed by a special spherically corrected lens[5] so that after passage through

[1] See F. E. Wright, Jour. Wash. Acad. Sci., *4*, p. 594; 1914; also L. H. Adams and E. D. Williamson, Jour. Wash. Acad. Sci., *9*, p. 609; 1919, for references.

[2] Phil. Mag., *20*, p. 740; 1910: also Engineering, *91*, p. 1; 1911.

[3] See Coblentz, Emerson and Long, Bull. Bur. Stds., *14*, p. 653; 1919.

[4] On this point, however, see F. E. Wright, Am. Inst. Mining Eng., Bull. No. 158; Feb. 1920.

[5] These lenses were designed and constructed for us by the Bausch and Lomb Optical Co.

the first nicol it converges to an image—circular spot about 4 mm in diameter—at the specimen under test. (See Fig. 1.) It then diverges through the second nicol to the second lens, which finally focusses it

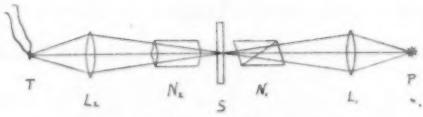


FIG. 1. *Diagram of apparatus.*

on the small circular thermopile. All the parts are mounted very rigidly on a heavy base as shown in Fig. 2, and a sensitive d'Arsonval galvanometer completes the equipment.

While there are some small difficulties associated with the use of non-parallel light, they are much more than compensated for by the

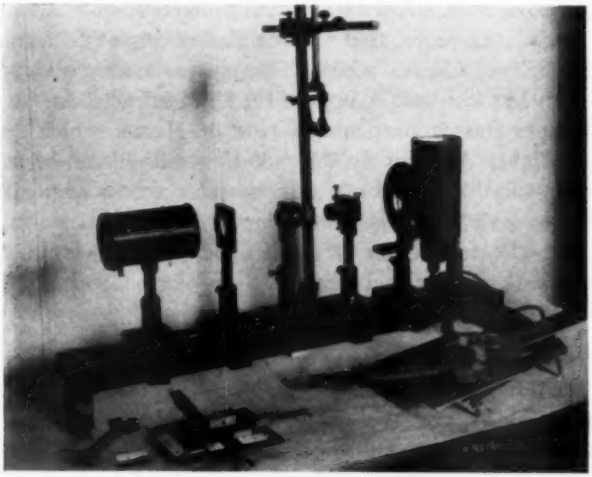


FIG. 2. *General view of apparatus.*

advantages of the present arrangement. One of these is that the area of the specimen under investigation at any one time is small. This is desirable since the strains due to poor annealing vary from point to point both in direction and magnitude. Another and more important advantage arises from the fact that, because the specimen is placed at the focus of a convergent beam, small surface irregularities have very ittle disturbing effect on the beam as it diverges again to the second

lens. This makes it possible to test pieces of glass with quite rough or crinkly surfaces. It is even feasible to work with specimens such as milk or opal glasses which scatter or diffuse the light greatly.

Operation. The apparatus is first carefully adjusted so that the nicols are exactly crossed, i. e., transmit a minimum of light. Partly because of the non-parallel light it is found impossible to reduce this minimum below about 0.1% of the incident energy. The specimen is then placed in position between the nicols and the galvanometer deflection noted, using a shutter for the zero. As it is obvious that the deflection will depend on the relative orientation of the direction of strain and the principal planes of the nicols, the specimen is mounted in a special holder (two of these are shown lying on the table in Fig. 2.) so that it can be rotated about the axis of the beam. The galvanometer deflections will then pass through maxima and minima 45° apart. From the maximum deflection, corrected as described shortly, the depolarizing action of the specimen and consequently its strain may be calculated.

Theory. The principles involved may be described briefly. Plane polarized light of azimuth 45° from the first nicol is incident on the specimen whose principal strains—two only are considered because of the relative thinness of the specimen and these are taken to lie in the plane of the surface—are vertical and horizontal. The birefringence due to the strain causes a difference of phase of the two components of vibration (vertical and horizontal) on leaving the specimen and this results in an elliptical vibration. The square of the component of this vibration in a direction at right angles to the original azimuth of polarization, i. e., *in* the plane of the analyzing nicol, determines the galvanometer deflection D.

To calculate the phase difference it is sufficient to know D and also D', the deflection corresponding to the combined energy of the two components which give rise to the ellipse. The most direct way—although for practical reasons not quite the one actually employed—of doing this is to insert the specimen so that the axes of stress are parallel to the principal planes of the nicols, and, with the nicols parallel, measure the energy. Then $(D/D')^{1/2}$ is a measure of the phase difference. For small ellipticities the phase difference is directly proportional to this square root: for larger ones a simple calculation is required. It is evident that the method is inapplicable for phase differences much exceeding a quarter of a wave length. Such, however, are rarely encountered in annealing problems unless the specimen is very thick or the strain excessive.

The phase difference per centimeter thickness of the specimen is taken as a measure of the strain. While an accurate numerical calculation of the actual stress would involve the knowledge of a number of other factors, an approximate computation is possible.[6] This gives, as the largest encountered in this work, stresses of the order of 100 kg per sq. cm.

Corrections. It might be expected that the minimum galvanometer deflection as the specimen is rotated about the axis of the beam would be zero. While this is nearly true for some specimens it is not the case for the majority. There are two reasons for this: One is the energy, as already mentioned, which passes the nicols even when they are exactly crossed. The other is a depolarizing action associated with scattering, which comes into account when the specimen has a rough surface (e. g., ground glass), or when the scattering takes place throughout the volume as in milk or opal glass. A study has been made of this point, in unstrained specimens, involving in some cases the "smoothing" of a rough surface by a drop of Canada balsam and microscope cover glass, and it is found that this effect is independent of orientation around the axis of the beam and hence can be readily separated from the effects due to strain. These two factors make up the minimum galvanometer reading, which would otherwise be zero. Consequently the net deflection obtained by subtracting the minimum from the maximum gives the quantity D used in the calculation.

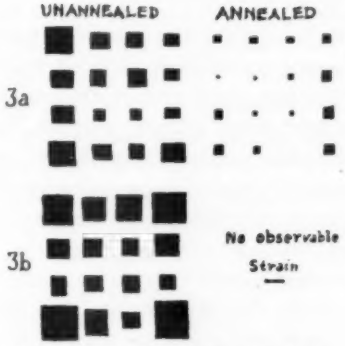
RESULTS

The results on some specimens about 5 cm square and 5 mm thick are shown in Figs. 3*a* and 3*b*. The strain, or rather the phase difference per unit thickness, is measured at points 1 cm apart and indicated in magnitude, on an arbitrary scale, by the area of the blackened square centered on each point. The difference between the annealed and unannealed specimens is striking. A few measurements have also been made on small pieces of glass whose strain was produced by compression or bending. Only enough has been done with these to indicate the possibilities of applying this method to interpreting the measurements in terms of actual mechanical stress, if desired.

In addition to these measurements on small plane pieces, a considerable number of tests have been made on rough surfaced diffusing shades. Because of their opacity, or rather their great scattering action, and the character of the surface these are more difficult to handle. A few sample

[6] For data see Adams and Williamson, loc. cit.

results are given in the accompanying table. The strains as stated are relative to a "standard," e. g., a certain Pyrex dish in which a small portion is indicated as having an allowable strain. While essentially



FIGS. 3a AND 3b. *Results on specimens.*
3a, specimen 642 B.G., opal glass
3b, specimen 706KY., diffusing glass.

arbitrary, such a standard is useful from a practical standpoint, in indicating the degree of annealing.

TABLE 1.

	Strains		
	Zone 1, central	Zone 2	Zone 3
10″ shade #2, unannealed	1.7–2.2	4.7–10.0	3.6–5.7
10″ shade #5, "	1.2–4.0	2.0–12.0	8.6–10.0
10″ shade #3, annealed	0.4	0.7	0.3
8″ shade "	0.2	1.0	0.8

We are glad to acknowledge our indebtedness to the Corning Glass Company for supporting the fellowship under which this work was done; and in particular to Dr. J. T. Littleton, Jr., who originally suggested the problem and who has furthered the work in every way possible.

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AUGUST 29, 1927.

A METHOD OF OBTAINING AN INTENSE BEAM OF LOW-VELOCITY ELECTRONS

By H. E. Farnsworth

Experiments which necessitate the use of a narrow beam of low-velocity electrons become increasingly difficult with a decrease of the velocity desired. The two chief factors to contend with are space charge and magnetic field of the filament current. In addition to these any external magnetic fields, such as the earth's, must be eliminated.

The usual well known method of overcoming space charge is to insert an extra grid or diaphragm to which the electrons may be accelerated and subsequently retarded by another diaphragm, so that some of the electrons pass on through apertures with an equivalent energy equal to the difference between the accelerating and retarding potentials. This method works very well when the above difference amounts to

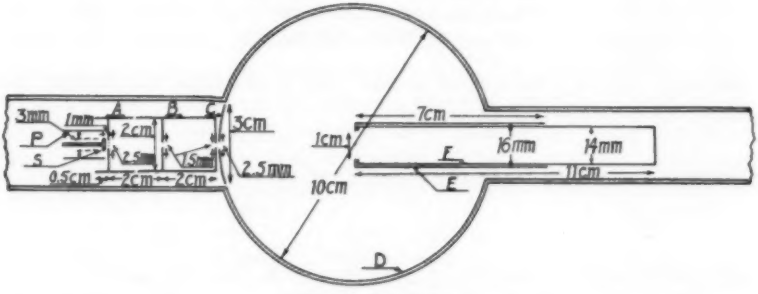

Fig. 1. *Apparatus.*

several volts but as the value of the retarding potential approaches that of the accelerating potential, the number of electrons which succeed in passing both diaphragms without appreciable change of direction decreases very rapidly. For any given difference, the number of electrons passing obviously depends on the actual magnitudes of the potentials used as well as on the geometrical configuration of diaphragms, size of openings, etc.

The method here described makes use of the accelerating and subsequent retarding fields but the usual diaphragms are replaced by cylinders of such design as to cause a larger number of electrons to pass than when the diaphragms are used. Fig. 1 shows a cross-section of this arrangement. The filament or cathode *S* consists of a strip

of platinum 3 mm wide and .013 mm thick, bent as shown, so as to be noninductive. The vertical part of S, which is oxide-coated, is the source of electrons. This is substantially an equipotential source since, with 3.0 amperes heating current, the potential drop across the vertical part is less than 0.1 volt. The accelerating potential for the electrons is in effect applied at the center of the source by a potentiometer arrangement across the battery terminals. The filament is surrounded by a platinum focussing cylinder P which is attached to the negative end of the former. A is a hollow metal (Cu in this case) cylinder containing a circular diaphragm near one end, the plane of which is perpendicular to the axis of the cylinder. This arrangement prevents electrons from passing from the cathode around the outside of the cylinder. 12 platinum wires of .025 mm diameter are evenly spaced over the 2.5 mm hole at the center of the diaphragm. B is a hollow cylinder with diameter equal to that of A, having diaphragms placed as shown. The diaphragm C forms a part of the sphere D. The diaphragms are all made of thin sheet platinum supported by thicker copper ring. The wires and diaphragms are blackened in a smoky flame to decrease secondary emission[1]. The inner surface of the glass sphere D is made conducting by sputtering with platinum. The Faraday cylinder F and shield E, having circular openings in the ends at the center of the sphere, permit a test of the uniformity of velocity of the electron beam in both magnitude and direction. The earth's magnetic field is compensated by Helmholtz coils of 1 meter diameter.

Electrons are accelerated to A, retarded to B, and pass on into the sphere with an equivalent energy equal to the accelerating minus the retarding potential. The design of A and B is such that the electric field in the gap between A and B is least uniform at the circumference while it is most uniform along the axis where the electrons pass. It will be noted that the distance between the diaphragm in A and the first diaphragm in B equals the diameter of the cylinders. No other dimensions have been tried but it is obvious, in approaching the two limiting cases which obtain as the ratio of these two distances either

[1] See Dalton and Baxter, Phys. Rev., *29*, p. 248, 1927.

During some observations on secondary electron emission the writer recently measured the emission from a smoked platinum surface and compared it with an unsmoked platinum surface. The ratio of the emission from smoked platinum to that from clean platinum is approximately as follows:

Primary energy in equivalent volts	2	3	5	8	10	15	20	40	100
Ratio of emission from smoked Pt to that from Pt	.39	.36	.35	.40	.43	.44	.44	.44	.49

increases or decreases from unity, that the electric field along the axis is less uniform than in the present arrangement. It seems probable that the field along the axis of two hemispheres (placed so as to form a sphere) at different potentials would be somewhat more uniform than that along the axis of the cylinders in the above case.

TABLE 1.

Equivalent energy of electrons—volts (corrected)	Potential of *A* with respect to *B*. volts	Current to *F*	Equivalent energy of electrons—volts (corrected)	Potential of *A* with respect to *B*. volts	Current to *F*
0.5	0	0	2.0	0	2.3
"	2	2.2	"	2	16.0
"	4	17.2	"	4	38.0
"	6	31.0	"	6	57.0
"	8	39.0	"	8	73.3
"	10	42.0	"	10	88.5
"	12	41.5	"	12	102.0
"	14	39.5	"	14	114.8
"	16	37.0	"	16	126.0
"	18	34.8	"	18	135.5
"	20	31.0	"	20	143.8
"	24	24.0	"	24	156.0
"	28	19.0	"	28	163.0
"	32	14.5	"	32	165.0
1.0	0	0	3.0	0	11.8
"	2	4.9	"	2	30.2
"	4	23.2	"	4	53.8
"	6	40.0	"	6	74.8
"	8	53.5	"	8	93.8
"	10	64.0	"	10	111.0
"	12	71.0	"	12	127.2
"	14	76.0	"	14	143.0
"	16	80.0	"	16	157.0
"	18	82.0	"	18	170.0
"	20	81.0	"	20	182.0
"	24	75.0	"	24	202.0
"	28	70.2	"	28	217.0
"	32	65.5	"	32	228.5

With the arrangement described it is possible to direct a beam of electrons into the Faraday cylinder *F* with a negligible amount of scattering, even when the average equivalent energy of the electrons is as low as 0.5 volt. To show the values of the electron current as a function of the potential of *A*, the corresponding values of these va-

riables are tabulated in Table 1 for four different equivalent energies. The units of current are in mm deflection of a galvanometer of sensitivity 4.1×10^{-10} amperes per mm on a scale at 1 meter distant. The filament current used is 3.0 amperes. The experimental procedure is to

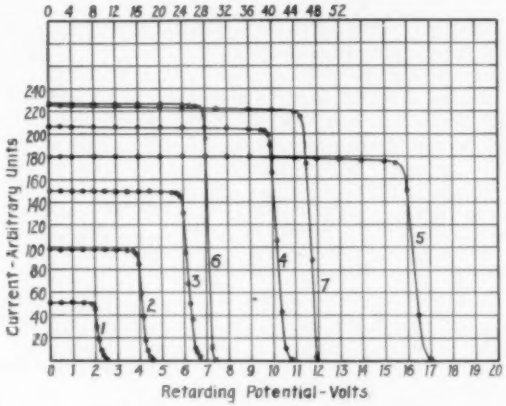

FIG. 2. *Velocity Distribution of Electrons.*

Curves 1, 2, 3, 4, and 5 are plotted to the lower and left scales. Curves 6 and 7 are plotted to the upper and left scales.

Curve	*1.*	*For resultant applied potential of*					*4.17 volts.*
"	2.	"	"	"	"	"	*6.23* "
"	3.	"	"	"	"	"	*8.32* "
"	4.	"	"	"	"	"	*12.43* "
"	5.	"	"	"	"	"	*18.8* "
"	6.	"	"	"		"	*31.2* "
"	7.	"	"	"	"	"	*50.0* "

connect B, C, D, E, and F to ground, with switches so arranged that the current to each of the above may be measured separately. S is then placed at some negative potential and the potential of A is given various positive values as in Table 1. This procedure accelerates electrons to A by varying amounts and retards some of them to B by smaller amounts, the difference in each case, however, remaining constant for each value of the equivalent energy. It will be noticed that, for the two lowest values of equivalent energy, the current increases with the potential of A to a maximum value and then decreases. For the other two the maximum lies beyond the observations shown. Hence, for low equivalent energies a relatively low potential difference between A and B causes the electron beam to scatter before entering the sphere

D. This is, of course, what happens when two diaphragms replace the cylinders *A* and *B* but to a much greater extent. The electron current can obviously be considerably increased by increasing the filament current without damage to the filament but 3.0 amperes was found sufficient for the present purpose.

The uniformity of velocity of the electron beam is shown in Fig. 2 for several different resultant applied potentials. The difference between this resultant applied potential and the average value of the equivalent energy from the curves is the correction due to initial velocity of the electrons, to finite resistance of the tube, and to contact potential between source and receiver. This correction is applied to obtain the equivalent energies in Table 1. The data for these curves are obtained by measuring the current to *E* and *F* as a function[2] of a variable retarding potential on *E* and *F*, all other conditions remaining constant. The filament current used is 3.0 amperes, although distribution curves obtained when using 3.5 amperes are equally good. The potential of *A* with respect to *B* is 8 volts. The homogeneity of the electron beam is surprisingly good, indicating that no appreciable emission occurs from the diaphragms which limit the beam.

The above arrangement makes it possible to carry out investigations with low-velocity electrons which were formerly impossible, such as the study of scattering of very low velocity electrons from metal surfaces for which it is being used at present.

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PROVIDENCE, R. I.,
AUGUST 20, 1927.

[2] Since a slight scattering to *E* occurs for the higher retarding potentials, the total current to *E* and *F* is observed.

ILLUMINATION IN METAL MICROSCOPY

By Harry S. George

ABSTRACT

An "ideal method" of illumination is advanced with specific means for its production in metallography. It is shown that it is deleterious to ocular perception and photography to illuminate with rays parallel or even nearly parallel to the line joining the object and the eye or the camera, not only for perception with the unaided eye but through the microscope. In metal microscopy axial light is deleterious because it produces an inferior image of lower resolution and definition and it also neutralizes the shading effect of oblique light thus rendering many details invisible by obliterating relief. Therefore, axial light should be eliminated and selected portions of the remaining hollow cone manipulated as described. Several types of apparatus are briefly discussed and an improved device is described. The article is illustrated by diagrams and by studies of grain structure in a solid solution.

ILLUMINATION

The importance of illumination in microscopy is well recognized. Quoting from a recent textbook by Barnard and Welch, "In photomicrography too much attention cannot be given to illumination for on this more than on any other factor depends the perfection of the result." It has been several years since the writer first published his method of illumination for the microscopy of opaque objects. Although several other workers, notably Dr. Carl Benedicks, have adopted it exclusively, yet it has not come into general use for at least three reasons. In the first place the apparatus described in the initial papers[1] was crude and difficult to manipulate. Furthermore, the introductory papers did not perhaps adequately explain the optical advantages of the method from the standpoint of illumination. Finally, it is possibly true that the new technique requires more skill and a better grasp of the subject of illumination than was formerly necessary. The present paper will attempt to remove these obstacles to the general adoption of the method by describing a more convenient device and by a discussion of illumination both in its broader aspects and, also, with particular reference to the microscopy of opaque materials, more particularly metallography. The reader is assumed to have a practical working knowledge of metallographic microscopy.

Ocular perception, especially that unaided by the microscope, is such a common natural function that we do not consciously analyze the process. In what follows some simple and obvious things will be stated with regard to illumination for ocular perception, general and microscopic.

[1] a. H. S. George, Trans. A. S. S. T., *4*, p. 140; 1923.
b. H. S. George, Trans. A. I. M. M. E., 1924.

A definition will be advanced for what is thought by the writer to be the best mode of illumination for practical vision and photography, whether aided by the microscope or not. This alleged best or ideal method will be compared with that found in nature and with the artificial systems heretofore adopted in microscopy.

Objects possess characteristics of form and color which enable them to be seen by the eye or recorded by the camera. These surface characteristics, however, would be invisible without light. Moreover, forms are not discernible, that is, not identifiable, and even invisible, no matter how intensely illuminated, if the light distribution is not properly arranged. The following specifications define what the writer considers to be the ideal manner of illuminating a body for the purpose of revealing its form. The light should preponderate from one direction with more or less diffused lighting from all other directions. The preponderating light should fall obliquely on the object and should preferably make an angle of 45° with the line joining the object and the eye. The preponderating light serves to produce definite shades and shadows. The diffused light reveals details in areas otherwise deeply shaded and softens contrasts. No other arrangement can be imagined that would better illuminate objects for the purpose of discernment by the eye, the camera or any other conceivable mechanism capable of detecting or recording light or forming an image, except for certain unique or special purposes. Nature has herself chosen this ideal method of illumination on the earth's surface at least.

The sun, the clouds, more diffuse moisture and dust, together with other more substantial objects, all play definite rôles in lighting any particular object. The sun, besides supplying the light, supplies it from one localized direction while other objects reflecting some of the light, produce a desirable diffused illumination. Other ways which nature might employ may be imagined but none that would be as practicable. A graphic representation of this natural and ideal mode of illumination is shown in Fig. 1. Things "look natural" because they are shaded definitely and cast definite shadows, both circumstances being desirably modified by diffused light. Whenever, as sometimes occurs, nature illuminates objects otherwise, as by directed with no diffused light or vice versa, things look unnatural, high lights are too strong, shadows are too deep, or there are no shadows. These appearances must be interpreted in the light of past experience. It is evident therefore, that the more closely artificial illumination can be made to approach the ideal commonly occurring in nature the more practicable it will be for us.

This applies to artificial lighting in connection with the microscope as well as that for the unaided eye. It also applies to such other aspects of the subject as the composition of the light itself but the present discussion is concerned only with illumination for the purpose of revealing form.

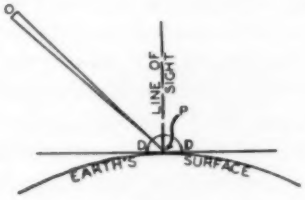

FIG. 1. *Vectorial representation of ideal or natural illumination. OP = intensity and direction of the predominating light (sun). DP = intensity and distribution of the diffused light.*

In the microscopy of opaque objects under medium and high powers, more specifically the metallographic examination of suitably prepared metal surfaces, light is necesssarily admitted to the object by way of the objective lens, whence it is reflected back as an enlarged image to the eye. The distance between lens and object may be too short to admit light from the sides or if light can be admitted the angle is so acute that plane areas on the object's surface reflect it outside the lens and they appear dark. The only practicable method for medium and

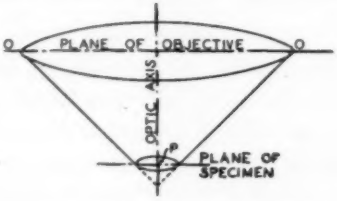

FIG. 2. *Diagrammatic representation of axial illumination. Full cone of light, axial and oblique, between objective and specimen.*

high power work is to admit light through the objective lens and for this purpose a device called an illuminator is used. The best type of illuminator, at least for high power work and the one now almost universally adopted, is the plane glass disc. This supplies a full conical beam of incident light (see Fig. 2) to the objective which functions as a condenser when illuminating the object. The incident light emerges from the objective in a converging, cone shaped beam whose apex theoreti-

cally coincides with the point at which the optic axis enters the object. The distribution curve is shown in Fig. 3, and should be compared with Fig. 1. Obviously this does not correspond to the illumination to which we are accustomed in nature and moreover is not a condition best adapted to our needs. The trained microscopist, however, adapts himself to it and learns to interpret what he sees in the same way that a machinist will interpret a mechanical drawing, reconstructing mentally what his intelligence teaches him the appearance represents. Furthermore, in a great many cases the details are neither resolved nor magnified sufficiently to reveal their true configuration even if they were illuminated more naturally and consequently this thoroughly artificial illumination is entirely practical in such instances. But for the study

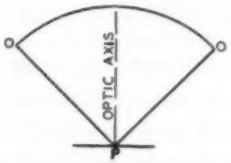

FIG. 3. *Vectorial representation of axial illumination. OP = intensity and distribution of the incident light.*

of structural details, when it is necessary to learn more than that certain constituents occupy certain areas it becomes highly desirable to modify the incident beam. This can be done in such a manner as to simulate almost identically the ideal natural mode described above.

APPARATUS

If all but an eccentric portion of the incident cone be prevented from entering the objective the object will then be illuminated more naturally. Thus, if an opaque disc is interposed at a suitable point in the beam its cross-section will appear crescent shaped (see Fig. 4). A hollow crescent shaped cone of light emerges from the objective. The midde of the crescent will then be the principal source of light (as the sun is), rays from it producing definite shading effects on resolved details. Fig. 5 is the curve of distribution of this system. When the complete beam is used, these effects are neutralized by the more axial rays or by diametrically opposed rays. The two cusps of the crescent (if the crescent extends more than 180°) serve as auxilliary sources of lower intensity simulating the diffused light found in nature and serve to soften shades and shadows, even revealing details of structure in shaded areas.

Instead of the opaque disc, a supplementary iris diaphragm may be used, placed eccentrically in the beam but the resulting illumination is too strongly uni-directional, producing deep shades and shadows. The same objection applies, though not to so great an extent, to the sector epiphragm proposed by Benedicks.[2] In this device, a certain optical advantage is claimed. This does not pertain, however, to the aspect

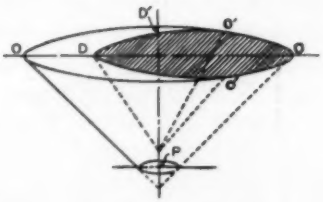

FIG. 4. *Diagrammatic representation of conical illumination. The opaque stop removes the axial and part of the oblique rays.*

of illumination already discussed but to a secondary aspect affecting the resolving power of the microscope. The word epiphragm is used by Benedicks to mean a stop for eliminating inner portions of the beam, as distinguished from a diaphragm, which stops out peripheral portions. Benedicks' sector epiphragm has its axis of rotation fixed and coinciding with the optic axis and possesses the advantages and disadvantages of rigid, precise construction. The method itself is very sensitive to lack

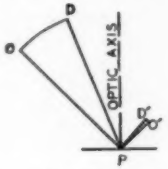

FIG. 5. *Vectorial representation of conical illumination. OP = intensity and distribution of predominating or oblique light. O'PD' = intensity and distribution of diffused light. Note similarity to* FIG. 1.

of symmetry in the optical train. It is desirable therefore to operate the epiphragm independently to allow of compensating for inaccuracies in adjustment or inherent unsymmetry in the optical train and not to have a fixed axis of rotation. However, if the optical train is precise and accurately adjusted the fixed axis of rotation is the logical thing. One of the author's first devices, not however of the sector type, had a fixed axis of rotation but it was found to be impossible to operate on

[2] C. Benedicks "Metallographic Researches," Chap V. (McGraw-Hill, 1926).

account of the practical difficulty of maintaining optical symmetry in the illuminating system. There would be no such objection to havng a fixed axis for the epiphragm if only a limited portion of the beam were to be utilized, for example, any or all of a given semi-cricular sector. But metal structures reveal much more detail and are more accurately depicted and interpreted if illuminated with oblique light capable of being rotated, as regards the direction in which the intensity predominates, completely around the optic axis. If this were not the case

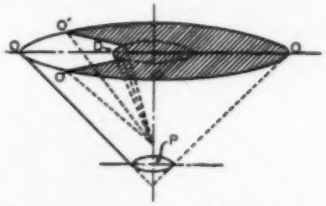

FIG. 6. *Diagrammatic representation of sectorial epiphragmmatic illumination. The epiphragm removes light from the cone in shaded area O'DO'O.*

then it would be simpler to use such a contrivance as that designed by Jewel[1] for producing conical illumination of a fixed type, where the direction in which the light strikes the object can not be changed.

The device which will now be described was designed to meet all the practical requirements that have confronted the writer. Its axis of rotation is independent or rather it has no axis of rotation, strictly speaking. It is intended for operation with the microscope preferred

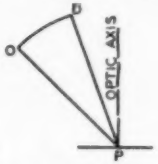

FIG. 7. *Vectorial representation of sectorial epiphragmmatic illumination. OPD=intensity and distribution of predominating light.*

and used by the writer, namely, the inverted type with automatic arc illuminant. The epiphragm is an opaque disc about 3/4 of an inch in diameter (experience has shown this size to be satisfactory for general purposes) mounted in a mechanical stage as illustrated in Fig. 8. For added convenience the disc is made to form an integral part of the usual light filter either by affixing to the filter a disc cut from opaque paper or by painting an opaque spot on it. The filter holder is held

[1] Jewell, Trans. Optical Society, *14*, p. 159.

in the stage and mounted as shown. The epiphragm is thus capable of independent motion in one plane, possessing two degrees of freedom.

It is desirable to place the epiphragm as shown so that its shadow and the light crescent on the light filter may be easily seen by the operator. This feature is a distinct aid in manipulation. If the disc casts a shadow on the object as observed through the microscope this should be corrected, for the specimen should be evenly illuminated even when a 3/4 inch disc is placed concentrically in the illuminating beam at the point shown, i. e., close to the front of the illuminator. If this condition

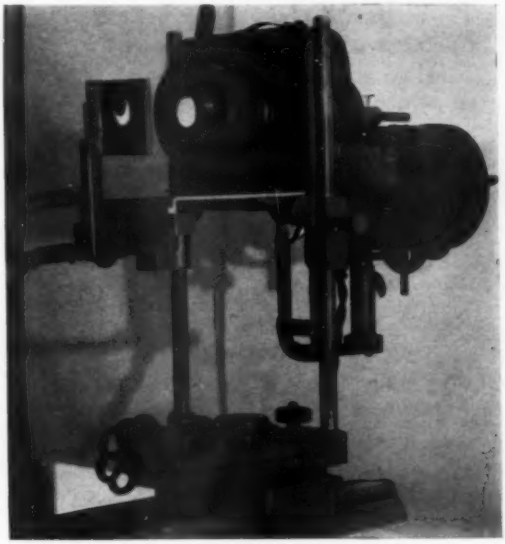

FIG. 8. *Apparatus for obtaining conical illumination.*

does not obtain then the disc can be moved along the beam until a point is found where the specimen is illuminated evenly. But since the best position for the epiphragm is as shown it is better to select a supplementary condenser of the proper focal length, to be found by trial for any particular instrument, rather than to move the disc from the preferred position. Where the illuminant is at arm's length from the microscope, as with most arcs, it may prove tiresome and awkward to operate the mechanical stage (carrying the epiphragm) by the usual knurled heads and these may be replaced by universal joints to which are fastened rods extending to within convenient reach of the operator as shown in Fig. 8.

RESOLVING POWER

Conical illumination has been given some theoretical consideration by Benedicks[4] and also by Pirk.[5] Benedicks points out the superior image forming ability of oblique light as compared to axial light and also shows that it has twice the resolving power. It follows that by stopping out incident axial light the image, which would otherwise be formed by it and superimposed on the superior image due to oblique light is eliminated. There results a more refined image capable of twice the useful magnification than was heretofore possible. This is a most interesting observation and is an entirely separate aspect of the subject than the matter of illumination per se. Pirk indicates the desirability of further study of the optics of conical illumination.

It would not further the purpose of this paper even if it were within the scope of the writer's ability to discuss the subject mathematically. In fact he has found no authoritative text which adequately treats the optics of metallography in a comprehensive scientific way and until this need is filled the subject must be considered as an art in which practice has taken several strides ahead of theory. The questions which the writer would like answered are:

(1) To what extent is Abbe's work and in fact any of the work on transparent microscopy, applicable to opaque microscopy?

(2) If the following formulas for resolving power are applicable to microscopy with reflected light, which of them should be considered in calculating the useful magnification when (a) a full conical illuminating beam is used (axial illumination) and (b) a hollow conical beam is used (conical illumination)?

$$\text{for vertical illumination } d = \lambda/\text{N. A.}$$

$$\text{for oblique illumination } d = \lambda/2\ \text{N. A.}$$

where d = smallest distance that may be resolved; λ = wave length in mm; N. A = numerical aperture of the objective.

(3) Should the normal (but trained) human eye be considered as limited to two minutes as the smallest angle for perception of detail.

STUDIES OF GRAIN STRUCTURE

The six studies of grain structure in Fig. 9 while interesting by themselves, metallographically, are shown primarily for the purpose of demonstrating conical illumination. A brief discussion of their structures may not be out of place. They were all taken at 1000 diameters with an oil immersion objective, a common 1.9 mm achromat, and

[4] C. Benedicks (loc. cit.)

[5] G. Pirk, G. E. Rev., *4*, p. 264.

represent an aluminum-copper alloy containing 5% of copper. The specimens were quenched and all of the copper is retained in solid solution. After polishing, they were etched with Vilella's reagent for aluminum alloys, a solution of one part nitric acid and two parts of hydrofluoric acid in five parts of glycerin. This has etched away the surfaces of the individual grains comprising the solid solution to different levels because of the difference in rates of attack due to differences in grain orientation. Between such grains the boundaries are sloping steps. Between grains of approximately equal level the boun-

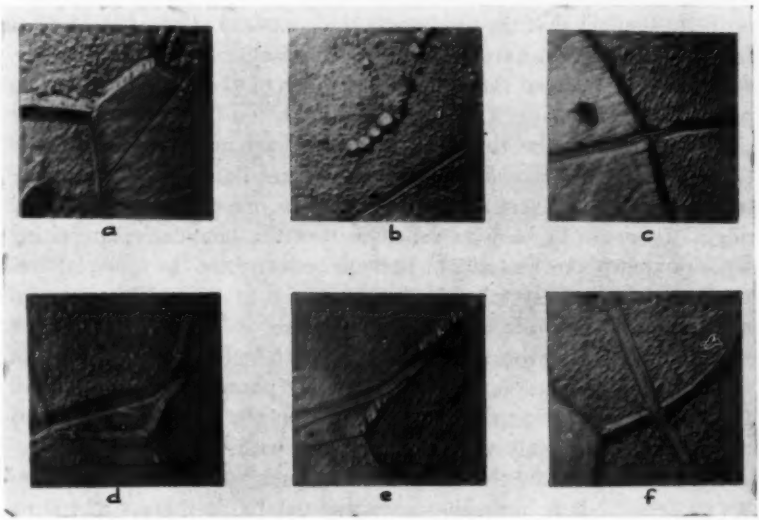

FIG. 9. *Studies of grain structure. Al-Cu alloy; etched; originally 1000 diameters, reduced one half.*

daries are usually A-shaped ridges. The pebbled appearance of some of the grains is due to the development of etching figures consisting of protuberances left in relief. They suggest another phase held in suspension in the solid solution but as none is known to exist under the given conditions, the small eminences are undoubtedly etching figures. All of the views show the path of a needle point that was drawn lightly over the polished and etched surface for the purpose of studying the relative hardness of the grains and their boundaries.

In Fig. 9*a*, the needle is seen to have been diverted slightly in its path downward to the left when it met the right hand boundary of the grain

which stands above the others. After cutting a furrow across this grain it jumps a little distance to the lower level of the next grain. In the rest of the views the needle was blunter and pressed a little heavier. In Fig. 9*c*, where the needle has met the grain boundary it is seen to have plowed a somewhat wider furrow indicating that the boundary is a ridge. This boundary has a longer and steeper slope to the right than to the left. When the needle met the ridge boundary in Fig. 9*d*, it was diverted sharply upward for the width of its own point before plowing through the boundary and proceeding to the next grain. The same diverting effect is shown in Fig. 9*e*. This diversion of direction is due to the fact that the needle met the boundary at an angle and not to any difference in hardness of the boundary material. From Fig. 9*f*, it may be inferred that the actual width of the grain boundary is probably much smaller than would be indicated by the width of the ridges or steps. Where the needle passes through and at right angles to the boundary the trace of the plane of the true boundary is seen. The truth may be that there are two such planes, one on either side of the ridge. It would be easy to conclude that the boundaries are either zones of amorphous material or perhaps zones where the space lattices of the contiguous crystal units are distorted and that this material is more resistant to the etching and therefore is left as a ridge. The evidence is not quite conclusive for either of these hypotheses, however.

In visual microscopic examination and photography by conical illumination the incident light is directed on the object from various angles. By successively viewing a field first with light from one direction and then from another and another, much additional information can be gained. It is sometimes advantageous to photograph the same field successively with light from different directions. In the case of the views shown the light was directed most advantageously to bring out the particular thing of interest. For example, in Fig. 9*f*, in order to reveal the trace of the grain boundary where the scratch enters the ridge it was necessary to direct the light parallel to the furrow.

When exhibiting or viewing photomicrographs taken under conical illumination it is helpful to orient them all alike and in such a manner that the high lights appear on the upper left of protuberances. Furthermore, the prints, oriented thus, should be examined under a good light directed from the upper left.

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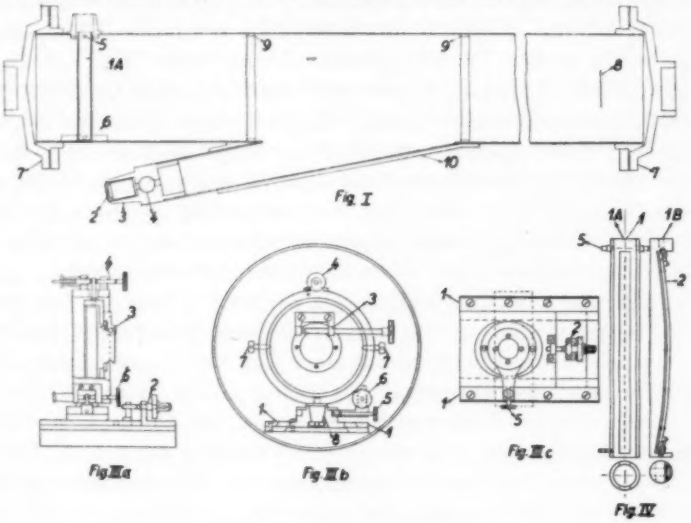
A NEW ONE METER VACUUM SPECTROGRAPH DESIGN

By Ralph A. Sawyer*

During the past year the writer has had occasion to design and put into use a vacuum spectrograph which seems to embody some novel and useful features and which, for vacuum spectrographic work in the region below λ3000, has proved so adaptable and convenient that it is described here in the hope that it may be of use to others.

In the design of this spectrograph the two objectives to be reached were: (1) that any type of vacuum light source might readily be used;



Details of vacuum spectrograph.

(2) that it might be adjusted with ease and precision. Attention was directed particularly, therefore, to the slit mounting, the grating mounting, the plate holder, and the vacuum seals.

The general layout is shown in Fig. I. It is somewhat like the Rowland mounting of the concave grating. The slit, 2, is mounted in a draw tube in the cone, 3, at the end of the side tube. By this arrangement plenty of room is provided for installing any light source before the slit. The light source may either terminate in a cone, fitting the cone, 3, or be cemented to an auxiliary brass cone fitting 3. Just behind the cone, 3, is a large stopcock, 4, having a bore large enough so that the entire grating may be illuminated by the slit. This cock serves as a shutter for starting and ending the exposure. When it is closed, the

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light source may be adjusted and treated at will, an essential with many vacuum light sources. This mounting of the slit also allows the spectrograph to be readily diaphragmed against stray light and leaves the camera end of the spectrograph proper free from all encumbrance.

The plate holder, 1 *B*, Fig. IV, is cylindrical, 20 mm in diameter, and is cut from a solid rod. The plate is held from behind and is bent by the cover, 2, to the focal curve of 50 cm radius. The cover, 2, is lined with one thickness of green billiard cloth. It is held in place at either end by sliding pins which engage slots in 1 *B*. The total length of the plate is 18 cm. Plates of .8mm thickness are used. These can be bent to the curve. The plate-holder slides into the tube, 1 *A*, in the spectrograph. This tube is pivoted at 5 and its other end slides on a way, 6, to which it may be clamped by a set screw. The plate holder is thereby pivoted about an axis which lies in the plate surface. A slot 1 cm wide is cut through the tube along its whole length, on the side toward the grating, to allow light from the grating to fall on the plate. On the other side a slot 3 cm long is cut at either end so that the specturm may be viewed from behind when the plate holder is removed.

The grating holder, Fig. III *abc*, is designed to hold the one meter concave grating ruled by the National Physical Laboratory, England, on a circular blank 72 mm in diameter. The whole mount is displaced along the axis of the spectrograph on the ways, 1, on which it is clamped by a screw and provided with a slow-motion, 2. The grating may be rotated about the axis of the spectrograph by the worm gear, 3. By the screw, 4, the grating may be rotated about the horizontal axis perpendicular to the spectrograph axis and by the clamping screw, 5, and slow-motion, 6, about the vertical axis. These three motions are all made about axes which pass through the central point of the grating surface. Thus any of the rotations may be made without altering the distance from grating to plate and to slit. This feature is of considerable value in facilitating rapid adjustments.

The slit is unilateral, with steel jaws 1 cm long, mounted in short ways and adjustable in width up to 1 mm. It is mounted on a short draw tube which is held fast in the cone, 3, by a set screw. For line spectra work the slit is adjusted to a width of .01 mm by aid of a micrometer microscope.

The spectrograph is closed at the ends by the large caps, Fig. I, 7, with conical ground bearings. These caps permit the spectrograph readily to be opened for adjustment and when greased with Leybold's extra-extra stiff Ramsay grease are perfectly airtight. The opening through which the plate holder is inserted is also closed by a conical

ground cap. Evacuation is effected through a 35 mm diameter glass tube with a ground joint fitting a cone on the spectrograph tube near its junction with the side tube. The only vacuum seals on the spectrograph are these three caps, the stopcock behind the slit, the cone which holds the light source before the slit, and the evacuating connection. The instrument is then closed wholly by ground joints and all difficulties with gaskets, cements, or waxes to close the spectrograph are avoided.

The main spectrograph tube and the side tube which carries the slit are made of drawn brass tubing with 2.5 mm wall. The main tube is 19 cm outside diameter and 120 cm long. The side tube is 7 cm in diameter. The rather large volume to be evacuated presents no difficulty to modern vacuum pumps. With a large Gaede three stage steel mercury vapor pump and Gaede oil forepump the spectrograph can be completely evacuated in 20 minutes. The ground cones, the stopcock seat and the supporting casting, 10, for the side tube are bronze castings. All joints are soldered. 9, 9 are brass re-inforcing rings. All parts are tinned inside and out both to insure air-tightness and to minimize the liberation of gases. The casting, 10, and rings, 9, make the whole spectrograph so rigid that it can be adjusted at atmospheric pressure and then evacuated without any detectable alteration in the sharpness of focus.

This construction permitted the diaphragming to be carried out very conveniently. With both end caps removed the slit was strongly illuminated. Then with the grating holder removed the side tube could be diaphragmed until the grating was fully illuminated by the slit, while light from the slit reflected from the side walls was eliminated. Diaphragms were found necessary at the back end of the slit draw tube, in the stopcock bore, and about 20 cm and 30 cm from the slit.

After the side tube had been diaphragmed the grating was placed in position. It was then only necessary to place diaphragms in the main tube until, as the grating was turned from side to side, an observer at the camera end of the tube could see that no reflection of the central image from the side walls reached the plate and could thus be certain that no light diffracted from the grating could reach the plate, save directly. Following this method four diaphragms of proper aperture were placed respectively 12 cm, 45 cm, 70 cm, and 90 cm in front of the grating. A horizontal diaphragm was also placed before the mouth of the evacuating tube. The diaphragms were made of brass, oxidized, and held in place by split rings.

To adjust the spectrograph a strong light is placed before the slit, and a ground glass screen is placed in the cassette holder, 1*A* Fig. I,

so that it can be viewed from behind through the previously mentioned slots in the back of this tube. The grating is now adjusted until the direct image of the slit is brought to a focus on the axis of rotation, 5 Fig. I, of the plate holder and the distances slit-to-grating and direct-image-to-grating are equal. These distances can be measured closely enough (to 1 mm) with a meter stick. The final focusing of the direct image is made photographically by the aid of small displacements of the slit draw tube.

One point of the curved plate (its axis of rotation) is now in focus. To complete the adjustment it is only necessary to swing the plate about this axis until one other point is brought to the focal curve. Then since the plate is bent to the proper curvature, the whole plate is in focus. To make this final adjustment the slit may be illuminated with a spark between one aluminum and one zinc electrode. With an uranium glass fluorescent screen approximate adjustment may be made on the strong lines near λ2500 Angstrom units. The final adjustment follows on the spectrum between λ3000 and λ1850. The entire plate length is now in focus and as mentioned above no noticeable change in adjustment is caused by evacuation. The adjustment in vacuum may be readily checked with a carbon vacuum arc. The whole adjustment is made at atmospheric pressure and may be made as easily and rapidly as the adjustment of a grating for the visible spectrum because all parts are visible and accessible and because the plate can be rotated about the direct image as axis. After the adjustment is completed the end caps may be greased and placed in position and the apparatus is ready for use in the region below λ3000. The normal to the grating falls near λ2000 and accordingly over the greater part of the plate the spectrum is nearly normal.

Plates as long as 100 mm have been successfully bent to the curve and a spectral region of 1700 Angstroms photographed on one plate. It should be possible, with slightly thinner plates, to fill the whole length of the plate holder with one plate. It has been found best, in inserting plates, to lay the plates in place and then insert one end of the retaining cover, 2 Fig. IV. The other end of the cover is then slowly brought into place. The plates, in the large majority of cases, take the curve satisfactorily. It has been found that if the plates do not break immediately they almost never break later during the exposure.

For much helpful advice on the design and for his kindness in permitting its construction in the Institute shops, I am indebted to President F. Paschen of the Physicalisch-Technische Reichsanstalt.

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A Short History of Physics. H. Buckley. Pp. XI+263. Methuen and Co. Ltd., Great Britain, 1927.

Aristotle taught that knowledge is gained by the inductive method by classifying and comparing individual events. He also taught that from the induction, further knowledge might be gained by deduction, which should, however, be tested by experiment. How, in the field of physics, he nevertheless fell a victim to preconceived notions; how, for nearly 2000 years, others followed him in these notions blindly; how, first Roger Bacon and later Francis Bacon sought to restore the original Aristotelian ideal, emphasizing the crucial importance of experiment, is the subject of the introductory chapter.

Other chapters in order discuss "Planetary theory, mechanics and the laws of motion; matter and the conservation of mass; the corpuscular and wave theories of light; the atomic theory of matter; the elastic solid theory of light; magnetism and electricity; heat and thermodynamics; the kinetic theory of matter; radiation; the atomic theory of electricity; the atomic theory of electricity (continued); the theory of relativity; the quantum theory; the structure of the atom."

It is surprising that so nearly all of the developments of physics can be classified under these headings. Some topics are not included, e. g. sound, hydrodynamics.

The arrangement differs markedly from that of other histories of physics. The author has paid much attention to points of view as they existed and has given clear statements in some detail of what the different individuals have contributed, often in their own words. Relatively speaking, the number of workers in physics which has been mentioned is small but the selection has been very good.

The author has paid no attention to the human traits of the workers nor to illuminating side-lights which accompanied their contributions. For instance, in connection with the corpuscular theory wave theory controversy, no mention was made of Hooke's rather savage criticism of Newton's early objections to his wave theory, or of the fact that Thomas Young, following the presentation of his first paper on the wave theory, was so severely criticized that the pamphlet he published in reply had but a single purchaser, or of Brewster's basing his opposition to the wave theory, on his inability to see why God should go to all the trouble of filling infinite space with an ether in order that "that twinkling little star" might send its light to us.

As a history of physics text, this book is needed; and the brief bibliographies given at the ends of the chapters will be greatly appreciated. As a

reference for the class room and the semi-scientific lecturer, it will be equally appreciated for its logical, evolutionary treatment of the main questions which have not only in the past but which now interest us greatly.

A. G. WORTHING